Scottish Universities Environmental Research Centre

DEVELOPMENT OF LUMINESCENCE TEST TO IDENTIFY IRRADIATED FOOD

FINAL REPORT : PROJECT N1701

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ABSTRACT

This is the final report of project N1701, commissioned by MAFF from October 1990 until March 1992. The principle aims of the project, at a time when statutory changes involving strict labelling rules were anticipated, were to consolidate the thermoluminescence technique already developed at SURRC and to investigate it's extension to fruits and vegetables.

The TL procedures for mineral separation were further developed by the incorporation of pre-concentration steps. These steps were introduced in order to improve the the sensitivity of the TL signal, particularly, where the separation technique resulted in low mineral yield for commercially clean samples. This has resulted in an order of magnitude increase in the absolute, TL, signal levels and provides a means of obtaining larger quantities of minerals for any further quantification, thus reducing the ambiguity of interpretation of data.

An EC interlaboratory trial was instigated, using the full mineral separation method with re-irradiation on a set of calibrated reference materials and paired (irradiated and unirradiated) samples of 12 commercial grade herbs and spices. Despite the diversity of experience and equipment employed, results from all laboratories showed that it was possible to determine which samples were irradiated. This demonstrated the strength of the separation method that its implementation could be successfully achieved in other laboratories. The procedure was then formally recognised and published, by MAFF, for detection of irradiated food for enforcement of UK legislation.

As the mineral debris responsible for TL in herbs and spices occurs ubiquitously on all foodstuffs, which have been exposed to wind and soil, investigating the application of TL to fruits and vegetables was a natural extension of the previous work. An extensive survey was conducted of TL signals from fruits and vegetables, including exotic varieties. Minerals were separated from duplicated pairs of irradiated and unirradiated samples of 22 fruits and 20 vegetables. TL results demonstrated unambiguous discrimination between irradiated and unirradiated vegetables provided that concordance diagrams were used. For soft fruits in particular water based separation produced more variable results. However, subsequent analyses using a full density separation with HCl wash were more successful.

It was recognised that whereas herbs and spices are largely protected from exposure to light during production and distribution, this is unlikely to be the case for fruits and vegtables. Since light exposure is known to reduce TL signal intensity, a set of illumination experiments was conducted to investigate the implications of optical bleaching for identification. Light boxes were constructed and characterised to simulated optical bleaching under controlled conditions. Two series of experiments were conducted with irradiated and control mangos. In the first experiment the effects of exposure to two different light sources at a level of 1 J cm^{-2} were investigated using 40 mangos. In the second experiment the influence of duration of exposure from 1 - 128 J cm^{-2} was examined for artificial daylight illumination of a further 96 mangos. The results of these studies show that although the TL signal is reduced as a result of exposure to daylight, there exists a residual unbleachable component comprising upto 40-50% of the original signal. In most cases the resulting TL will be distinguishable from background levels.

As a result of this work it is now possible to extend TL detection protocols to a wide range of fruits and vegetables. Providing that recontamination with unirradiated minerals has not occurred after irradiation, the majority of treated fruits and vegetables are expected to be detectable. Positive signals will imply an irradiation treatment. There remains some possibility of false negative results from a small proportion of irradiated products.

Contents

1 Introduction

This is the final report of project N1701, commissioned by MAFF from October 1990 until March 1992 with the principal aims of consolidating the use of thermoluminescence techniques to identify irradiated herbs and spices, and to investigate the extension of this approach to fruits and vegetables. During this period statutory instruments were placed before parliament permitting the controlled application of irradiation to commercial food processing, subject to licensing conditions (SI,2490), and to strict labelling regulations (SI 2489). Unambiguous tests to detect irradiated foodstuffs are needed in support of both regulatory framework and labelling rules.

1.1 Effects of Food Irradiation

The use of ionising radiation to preserve foods was first suggested at the end of the last century, however large scale investigations into the effects of irradiation on foods did not take place until after the second world war when advances in isotope production and radiation technology paved the way for practical applications. A considerable corpus of research knowledge has been accumulated since this time, largely focussed on the physical, chemical and biological effects of ionising radiation on food (e.g. Urbain, 1986; Josephson and Peterson, 1983; Elias and Cohen, 1983), and also on the safety of irradiated foods. The physical processes of ionisation occur throughout the volume of an irradiated product, a concentration of ion pairs being generated in a manner which is largely independent of dose rate and process conditions. The primary concentration is however strongly dependent on absorbed dosed, which is the principle process variable. The chemical and biological effects of food irradiation arise as the consequences of the subsequent interactions of the direct ions pairs, generating charged molecular fragments, free radicals, and excited molecules whose behaviour is strongly dependent on process conditions. Process temperature, redox conditions, moisture content and dose rate all influence the diffusion characteristics and subsequent interactions of radiolytic products.

The effects of greatest interest in food processing are those which inhibit metabolic processes involving ripening and spoilage of fruits and vegetables, and the dramatic reductions to vegetative microorganisms which can be achieved with radiation exposures below 10 kGy. At doses below this level the energy deposition amounts to less than 3°C heat equivalent, and primary ionisation concentrations of the order of 100 ppm. In comparison with other preservative technologies irradiation leaves food in a condition which closely resembles the natural product, with few of the changes to colour, texture, flavour and nutrients associated for example with canning or freezing. The main applications of food irradiation and typical absorbed doses associated with these changes are tabulated below.

Table 1.1 Main applications of food irradiation

Purpose	Dose (kGy)
Inhibition of sprouting	0.05-0.15
Delaying Ripening	0.5 - 1
Insect Disinfestation	0.15-0.5
Shelf life extension	1 - 3
Elimination of spoilage and pathogenic organisms	1 - 7
Improving organoleptic qualities	2 - 7

1.2 The Regulatory Framework

Research into food irradiation, and particularly the safety or irradiated foods has been reviewed and coordinated internationally by the United Nations Food and Agricultural Organisation (FAO), the International Atomic Energy Agency (IAEA) and the World Health Organisation (WHO). Following research and the publication of, generally positive, safety conclusions (FHO/WHO, 1981, 1983), a Codex Alimentarius standard was published, recommending conditions under which food should be irradiated and plants operated. This document defines the concept of good irradiation practice. Adequate dose control, proper physical segregation of treated and untreated products, assuring the microbiological quality of products for treatment, and adherence to labelling rules fall within this category. A separate UK review committee endorsed the safety case for food irradiation (ACINF,1986, 1987) and recommended that the earlier prohibition on commercial food irradiation in the UK be revoked. A period of public consultation followed, during which time a considerable body of evidence emerged from the media and consumer groups indicating a generally antipathetic attitude from the public. Concern was articulated about possible commercial abuses of the process, and anxieties expressed concerning the credibility of labelling. A framework was however introduced as expected during the course of this contract, in the form of statutory instruments under the 1990 Food Safety Act. SI 2490 "The Food (Control of Irradiation) Regulations" came into force in January 1991, and introduced a system of licensing whereby seven classes of foods could be irradiated, subject to conditions which essentially enforce the Codex Alimentarius concept of good irradiation practice. The license condition impose a stringent set of protections against the types of abuse which appear to have caused public anxiety, and are arguably the most demanding conditions imposed in any country.

The food classes and their dose limits are shown below in table 1.2. Reirradiation is prohibited. In this instance the dose limits are for mean absorbed dose within the product under industrial radiation conditions, whereby spatial dose variation of up to +-50% is accepted. The food classes themselves are compatible with 1989 EC proposals (House of Lords, 1989), with the exception of fresh meat which was not included in the UK list. The present position within the EC is not harmonised, individual member states maintaining diverse regulations ranging from prohibition (eg Germany) to liberal authorisation (eg

Netherlands, Belgium, France). The position within SI 2490 is that licensed UK companies wishing to export irradiated foods within the EC must comply with national regulations for the destination country, and that irradiated imports from EC member states, or other countries should be of comparable safety to products which would have been licensed in the UK.

There is an additional obligation in the UK for explicit labelling of all irradiated foods (SI 2489) to be applied at all points of processing, distribution and sale - including on restaurant menus. Acceptable wording includes "irradiated" or "treated with ionising radiation", either on the whole product or on the list of ingredients as appropriate.

Table 1.2 The permitted food classes and dose limits under SI 2490

Foods	Overall Dose (kGy)
1. Fruit	up to 2.0
2. Vegetables	up to 1.0
3. Cereals	up to 1.0
4. Bulbs and Tubers	up to 0.2
5. Spices and Condiments	up to 10
6. Fish and Shellfish	up to 3.0
7. Poultry	up to 2.0

Internationally there is considerable variation in regulatory frameworks. An IAEA review in 1991 has ascertained that 24 countries worldwide either control the manner in which the process is applied or regulate the sale of irradiated foods. Another 7 or more countries are engaged in irradiation without national regulation. Of those countries regulating the process 5 do not require labelling to indicate that the process has been used, and the others range in requirements from a logo - the "radura" symbol to an explicit label. The UK labelling requirement is the most clear of any national regulation, and is intended to provide a basis for informed consumer choice. The need for laboratory tests to identify irradiated foods

arises in support of the labelling regulations, particularly for products which are traded internationally between countries with diverse national regulations. The need for enforceable labelling, and consequent requirement for laboratory tests became clear in the UK following the 1986 ACINF report. It is notable that IAEA have also subsequently recognised that public acceptance of food irradiation is predicated by confidence in labelling, and have established a programme of coordination of research into analytical detection methods (ADMIT).

1.3 Luminescence Detection Methods

Successful laboratory tests to detect irradiated foods require a radiation-specific property, which is produced when the product is exposed to ionising radiation, is preserved during product distribution and storage, and can be measured reliably in the laboratory, preferably at low cost and with high sensitivity. Thus three stages are involved in the detection process - signal generation, storage and measurement. Given a suitable phenomenon, a laboratory protocol is needed which can demonstrate unambiguously that any positive signals observed have genuinely originated from the test sample, and that negative results are due to the sample not having been irradiated rather than to a lack of sensitivity. These general conditions require careful attention to the measurement of laboratory blank levels, and most probably incorporation of radiation sensitivity measurements into the analytical procedure.

Many physical, chemical and biological effects are under investigation; some with promising empirical results. It is likely that those which ultimately succeed in becoming established tools will satisfy the general conditions outline above, including the procedural requirements.

Of the physical detection methods so far proposed, stimulated luminescence techniques have shown the greatest potential for sensitivity and radiation specificity. The three stages discussed above can be identified as energy transfer during irradiation, which generates free charge carriers in dielectric media some of which can be localised in metastable states with residual energy. During storage, the retention of trapped charge carriers involves energy storage. The final measurement step following stimulation involves release of excess energy in the form of light. The direct manner in which the required three stages can be equated with transfer of electromagnetic energy leads to the radiation specificity of these phenomena.

The use of single photon counting photomultipliers to detect radiation induced luminescence provides great sensitivity.

Thermoluminescence was first applied to the problem of identifying irradiated foods, in an attempt to improve on the capabilities of lyoluminescence (Ettinger et al., 1977, 1978) from sacharides and carbohydrates and chemiluminescence from spices (Bogl and Heide, 1984a,b; 1985; Heide and Bogl 1985b). Commercial TL dosimetry equipment was used to record glow curves from "whole samples" whereby complete herbs and spices were placed in direct contact with a TL heating plate (Heide and Bogl, 1985a, 1986, 1987), and used to record TL intensity. This approach provided much better discrimination between irradiated and unirradiated herbs and spices than available from chemiluminescence measurements, despite some obvious drawbacks from a metrological point of view.

Work at SURRC on the development of luminescence tests to identify irradiated foods began in 1986. An initial feasibility study confirmed that TL could be recorded from whole samples of herbs and spices, and also that strong signals were available from inorganic components associated with food (Sanderson and Izatt, 1987). The hypothesis that adhering silicates were responsible for the TL signal from herbs and spices was advanced at this time. Initial efforts under project N384, were concentrated on establishing reference measurements from a wide range of herbs, spices and seasoning mixes. TL measurements were taken from 5-10 mg aliquots secured with silicone grease to stainless steel discs and heated at 6°C s^{-1} in a research grade TL oven equipped with single photon counting. Whole samples results for over 160 samples confirmed that the majority of herbs and spices showed TL characteristics which did not depend markedly on the sample variety, and varied in sensitivity over more than 3 orders of magnitude. The background signals from unirradiated control samples also varied by up to two orders of magnitude. Although TL intensity measurements alone could discriminate roughly 94% of irradiated samples from blanks, these results showed that the whole sample approach suffered from poor reproducibility and a tendency to give false-negative results from low sensitivity samples. Attempts to improve whole sample discriminating power by using renormalisation, proved partially successful, but still left an undesirable level of ambiguity for low sensitivity samples. Despite these limitations encouraging results were obtained from a set of 45 herb and spice samples distributed by the Neuherberg Institute fur

Strahlenhygiene as part of a blind European interlaboratory study was undertaken in 1987 (Heide and Bogl, 1988). Using the whole sample technique with the addition of glow shape indicators and the SURRC reference data set, it was possible to identify all 45 samples correctly. However the reference set indicated that this assemblage of samples did not include problematic low sensitivity specimens.

It had been assumed by other research groups that the TL signals recorded from herbs and spices arose from major organic components without any firm basis for making such an assumption. An early priority therefore was to establish the origins of the TL signal.
A technique was therefore developed to separate any mineral components from the organic sample by ultrasonic agitation in a high density solution, (sodium polytungstate prepared to a density of 1.7 g cm^{-3}) followed by centrifugation to separate the organic and mineral fractions. The milligram residues were treated with HCl to remove carbonates, washed several times in deionised water, resuspended in acetone and deposited by sedimentation on stainless steel discs before TL measurement. The results immediately showed a 3 order of magnitude enhancement of TL sensitivity in the mineral phase, compared with organic residues, and an improved signal to background ration due to suppression of spurious chemical effects arising from heating the organic components. Further benefits of using such mineral separates were the ability to obtain comparable material from diverse sample types, without the need for extensive reference collections, and the ability to measure sensitivity by re-irradiation and second glow measurement following the initial TL readout.

Earlier experimental work using the density separation technique had indicated the need for very high laboratory cleanliness to avoid cross-contamination of minute particles with contrasting sensitivities. Stringent cleaning processes were carried out on all apparatus and reagents used in the separation, and checks made for blank levels. It was necessary to isolate individual sample discs during gamma irradiation to prevent cross contamination. Once these precautions had been added in to the procedure results from a large set of herbs and spices clearly showed that the TL signal was concentrated in the mineral phase, and that unambiguous discrimination between irradiated and unirradiated samples could be achieved by measuring this phase (Sanderson et al, 1989a,b,c, 1990).

The improvement in discrimination between samples which had previously shown diverse whole sample behaviour was achieved partly by isolating the component which carries the TL signal, and partly by measuring and correcting for variations in specific TL sensitivity from sample to sample using a re-irradiation method. The TL recorded for each sample in the first glow was normalised to that induced by a fixed gamma dose administered before the second TL measurement, to account for sensitivity variations. Although this introduces an extra set of measurements to the test procedure, there was clear evidence from over 85 different samples that ambiguities, particularly false negative results from a minority of low sensitivity samples, would be incurred without this step.

The results of this work attracted considerable international interest, our conclusions on the origins of the signal being rapidly confirmed by laboratories in Finland and Germany. There was however initial reluctance from some laboratories to adopt a methodology which gained reliability at the expense of laboratory simplicity. Nevertheless at the outset of this project it was already true to say that herbs and spices, possibly the most important class of irradiated foods and one which is subject to extensive international trade, could be detected without ambiguity.

1.4 Aims and Scope of the Project

The principle aims of the project, at a time when statutory changes involving strict labelling rules were anticipated, were to consolidate the thermoluminescence approach outlined above, and to investigate it's extension to fruits and vegetables.

The consolidation of TL testing for herbs and spices entailed three distinct actions; the incorporation of simple pre-concentration steps to enhance signal levels and reduce blanking problems, conducting an EC interlaboratory study of the use of mineral separation, and finally preparation of a test protocol acceptable to MAFF for the purposes of supporting UK regulations. This work is described in chapter 2.

The mineral debris responsible for TL in herbs and spices occurs ubiquitously on all foodstuffs which have been exposed to wind and soil. The possibility that a similar approach

might be successfully applied to fruits and vegetables was therefore recognised at an early stage. Investigations on potatoes and avocado pears in 1987 and 1988 suggested that it might be possible to obtain sufficient mineral material to enable TL testing. Brief investigations of the TL from strawberry skins had also been carried out in Germany (Heide et al, 1989, 1990), again the most likely signal origin being inorganic material adhering to the surface. To examine the potential of measuring signals from fruits and vegetables an extensive survey of exotic varieties was conducted using a modified version of the density separation technique. These results, which are extremely encouraging, are discussed in chapter 3. Finally it was recognised that whereas herbs and spices are to a large degree self-protecting from signal losses include by exposure to daylight, this may not be so for fruits and vegetables at certain stages of production and distribution. Therefore a set of illumination studies were conducted to investigate the dynamics and implications of optical bleaching for TL testing of irradiated fruits. These results are presented in chapter 4. The project conclusions are presented in chapter 5, which gives an overall view of the completed phases.

2 Development of the TL Procedures for Herbs and spices

Work was undertaken at the outset of the project to consolidate thermoluminescence procedures for detection of irradiated herbs and spices. Work under project N384 had explored the possibilities of avoiding the need for re-irradiation by using mass-normalisation; however although the discrimination rate from mass normalised mineral extracts was greater than from whole sample measurements there were still problems with low sensitivity samples. A further effort was made to examine the possibility of using an internal normalisation technique whereby the TL signal at 200-250°C (the metastable region where recent food irradiation dose are dominant) was expressed relative to the residual geological signal from around 400°C. This gave quite promising results, certainly as good as mass normalised data, but replaced variance in sensitivity with the almost equally great variability in residual geological signal from large sample sets. It was therefore concluded that the full procedure, originally published in 1989 remained the preferred method to obtain clear results.

Enhancements were made to the procedure by introducing pre-concentration steps, described below. Further attention has been given to stability, and in particular to the glow shape changes which occur during storage, and which have potential to provide some indications of post-irradiation storage conditions and detection of re-irradiation. In 1991 a short interlaboratory trial of the full SURRC procedure was conducted through BCR (Community Bureau of Reference). The successful results of this work led to the formulation of a formal procedure, published by MAFF which incorporates explicit quality assurance measures, and is presently the standard method for detection of herbs and spices in the UK. These developments are outlined below.

2.1 Introduction of pre-concentration steps

The original procedure consisted of direct ultrasonic agitation of several hundred mg. of herb or spice in centrifuge tubes filled to half height with sodium polytungstate solutions. Subsequent centrifugation and physical separation yielded the mineral extract which was cleaned up with HCl, washed in deionised water and deposited on disc from acetone as described briefly above. The mineral content of spices ranges from a few percent by weight

in the case of dirty samples to a small fraction of a percent from clean examples. Therefore the original sample sizes frequently produced sub-milligram extracts. Although the TL sensitivity was normally adequate to detect 5-10kGy doses from such small samples, it was recognised that the task of achieving freedom from significant laboratory contamination (from ambient dust, building materials etc) would be greatly eased by increasing the original sample mass.

Two extensions to the separation procedure were therefore implemented in 1990 to achieve this aim. The first was to acquire a larger centrifuge rotor and tubes able to separate 1 g. samples. This was entirely successful, but reduced laboratory throughput by utilising more space and heavy liquid per run. The second approach was an aqueous pre-concentration, whereby 10 g. or more of material was agitated ultrasonically in water to free attached mineral grains, and then rapidly sieved through 125, or 250 micron disposable nylon mesh to produce a concentrate with the majority of the fine mineral debris together with finer organic fractions. Experiments with various mesh sizes (90μm, 125μm and 250μm) were undertaken. It was found that finely ground spice samples can clog the finer mesh sieves. The 250μm mesh size proved to give the best yield of mineral grains. After Stokes settling and removal of supernatant water this concentrate was transferred to a centrifuge tube for density separation, subsequent steps being as before. This approach has been successfully adopted for routine use in the laboratory, and has resulted in one order of magnitude increases to absolute signal levels. It has the benefit of being scalable to any desired sample size, and therefore provides a means of extracting the 50-100mg quantities needed to apply standard additive dose procedures for quantification of exposure.

Two further benefits have been noted since the introduction of pre-concentration. Herbs and spices are frequently subject to high infestation and microbial loads. With increasing food hygiene standards appearing in the developed world many new methods are emerging to "cleaning up" herbs and spices, and we have seen the effects of these new methods in samples which were tested both from retail and trade sources. The number of minerals obtained from commercially processed clean samples is reduced. So it has been possible to overcome the associated analytical difficulties by the introduction of pre-concentration procedures. The second benefit is that by increasing the absolute signal level it is possible

to contemplate the use of conventional TLD readers, using anode current integration rather than photon counting, for analysis of bright samples.

2.2 Stability and glow shape changes during storage

Given the discriminating potential of thermoluminescence of irradiated samples, signal stability becomes an important consideration. Extensive whole sample stability tests were performed at an early stage, confirming that stability is not an obstacle to qualitative testing. It was also noted that glow curve shapes were modified during storage, and therefore a short series of investigations was initiated to investigate the potential information on storage temperature and duration available from TL glow shape analysis. There may be further potential for using glow shape analysis to identify re-irradiated samples.

The stability of TL from silicate minerals has been widely studied in the context of TL dating studies (Sanderson, 1988). The TL signals are composed of a pseudo-trap depth spectrum - higher temperature components generally originating from deeper traps within the crystal band gaps. Thermal fading from single trapping species may follow first order kinetics characterised by a mean life τ given by

$$\tau = s^{-1} \exp (E/kT_s)$$

where E is the trap depth, k is Boltzmann's constant, T_s is the storage temperature, and s a frequency factor.

For poly-mineral samples, or feldspathic minerals with broad distributions of trap depths losses due to thermal fading can in principle be described by summations of such first order components - therefore showing a composite non-exponential decay with time and complex storage temperature dependence. Fractional glow analysis coupled to Arrhenius transformation to analyse trap depths in these circumstances yield thermal activation energy spectra crossing from about 1 eV to 1.6 eV corresponding to the glow curve from 100°C to 500°C. Associated frequency factors are of the order of 10^{12} - 10^{13} s^{-1} resulting in mean life estimates at ambient temperature ranging from a few hours (for the

100°C ordinate) to over 10^7 years at the top of the glow curve. Thus the glow curve itself denotes a stability spectrum based on first order kinetics.

In addition to thermal losses however, a number of additional processes, including quantum mechanical tunnelling between trap and re-combination centre have been postulated, [35,36,37,38] to account for short term athermal losses originally called "anomalous" fading.[39] These proximity effects - if present - are expected to be more prominent at high doses than low doses for statistical reasons, and would give rise to a hyperbolic time dependent signal loss which does not depend markedly on sample storage temperature.

Given the certainty of multiple component signals, and the possibility of both thermal and athermal fading processes operating at low rates, empirical investigation of signal stability is essential. Long term stability tests were conducted, initially using whole samples, but more recently with pure mineral examples. The procedure adopted used parallel batches of irradiated and unirradiated controls stored at 4 different temperatures -20,5,30,and 55°C, and taking matched readings for samples and controls at logarithmically spaced time intervals from 3.5 days to 2 years. Additional samples were spread in thin layers and exposed to daylight at ambient temperatures to investigate the influence of optical bleaching.

Despite the expected variability of whole sample measurements these fading tests provided evidence that thermal losses dominate, although athermal processes may occur as a minor feature in frozen storage. The extent of signal loss with time depends both on glow curve temperature, and storage temperature - in keeping with expectations. Long term progressive signal losses were most clearly seen in the 200°C glow ordinate from samples stored at 55°C -the rate of loss at the 250°C ordinate being an order of magnitude lower. Losses at this latter glow temperature were of negligible importance at lower storage temperatures, and for samples with good initial signal to background ratios fading would not pose obstacles for correct identification. Figure 2.1.1 shows a whole sample fading test for Cayenne Pepper to illustrate most of these points. Initial signal losses from samples exposed to light were more pronounced, and could lead to false negative classification if the whole sample approach, with it's variable signal to background ratios were adopted. However the rate of bleaching diminished rapidly leaving a durable unbleached component which may still be sufficient to

secure qualitative identification using mineral separates. For herbs and spices this problem does not arise since they are generally opaque and are clearly damaged beyond use or value by exposure to the levels of light needed to effect TL signals. However the influence of optical bleaching will need further consideration with respect to other sample types which may be investigated.

It should be noted that storage for prolonged periods at 30-55°C produces damage to herbs and spices well before the TL signal has been eroded to an extent which would compromise reliable detection. It was also clear from these whole sample observations that the majority of signal losses occurred at the low temperature side of the glow curve. This is an expected consequence of the distribution of traps of different energies which lead to the broad glow curve peaks observed in TL measurements of polymineral silicate mixtures. Glow curve shapes are modified during storage as a direct result of the mixture of thermally astable, metastable and stable components in the TL glow curve. Examination of glow curves from whole sample storage tests confirmed the general trend of loss from the low temperature side. However the variations in thermal contact from sample to sample, and inability to normalise glow curves from individual aliquots, inherent to whole sample measurements, precluded a detailed analysis of the dynamics of TL glow shape modification.

A model experiment was therefore conducted to isolate these shape changes using a pure microcline (K-feldspar) sample isolated from a geological hebridean pegmatite. The microcline extract was crushed and sieved to 90-150 micron grains size and dispensed onto a series of 1 cm diameter x 0.25 mm thick stainless steel discs, coated with Electrolube silicone resin. Each of the discs was given a dose of 1kGy in the Cobalt-60 source and six hours following irradiation the thermoluminescence of each disc was measured to obtain a normalising value for each disc (to account for disc to disc sensitivity variations). The discs were then repacked and reirradiated to 1kGy for the storage tests. Immediately following irradiation five discs were stored in the dark at 5,30 and 55°C. Two discs were read out after a delay of six hours in order to record the initial unfaded TL signal. This six hour delay was to allow room temperature phosphorescence present immediately after irradiation, to decay to background levels. One disc was selected from each storage temperature after storage times of 1,3,7,14 and 28 days following irradiation and the remaining TL was measured.

Corrections to the glow curves were required to account for variations in the TL sensitivity of each disc. This was done by multiplying each channel in the glow curve by the ratio of the average sensitivity of the initial normalising glow curves to the sensitivity of the individual normalising glow curve. The sensitivity was determined from the integrated TL signal from 100 - 250 °C. Thus each measured glow curve was transformed to a standard brightness, equivalent to the mean sensitivity of all the discs used. The standardised glow curves recorded on days 1, 3, 7, 14, and 28 respectively are shown in figures 2.1.2 to 2.1.4. In each case the glow curve modification, loss of signal from low temperature ordinates can be clearly observed. It is also clear that the initial losses from lower temperature ordinates occur more rapidly than subsequent movements, and that higher storage temperatures lead to greater initial losses. The low temperature side of each glow curve (i.e. the initial rise) follows arrhenius form, and represents the thermal activation energy of the shallowest trapping component remaining at each stage. Therefore the changes in glow curve shape correspond to modification of the populated trap distribution by thermal leakage. Above the initial rise region the curves are very similar.

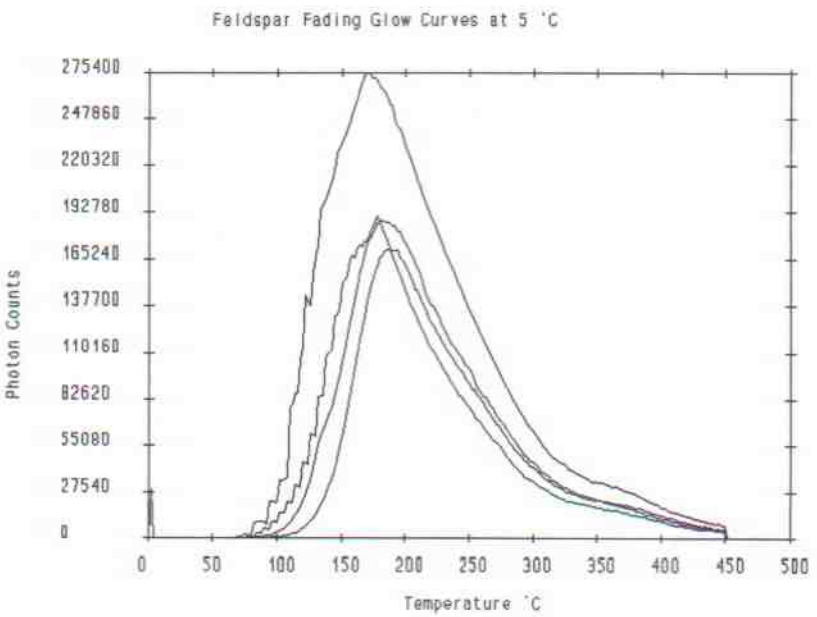

Figure 2.1.2 Standardised glow curves from microcline feldspar stored at 5°C and measured on days 1,3,7,14 and 28 following irradiation. Storage time increases from left top right.

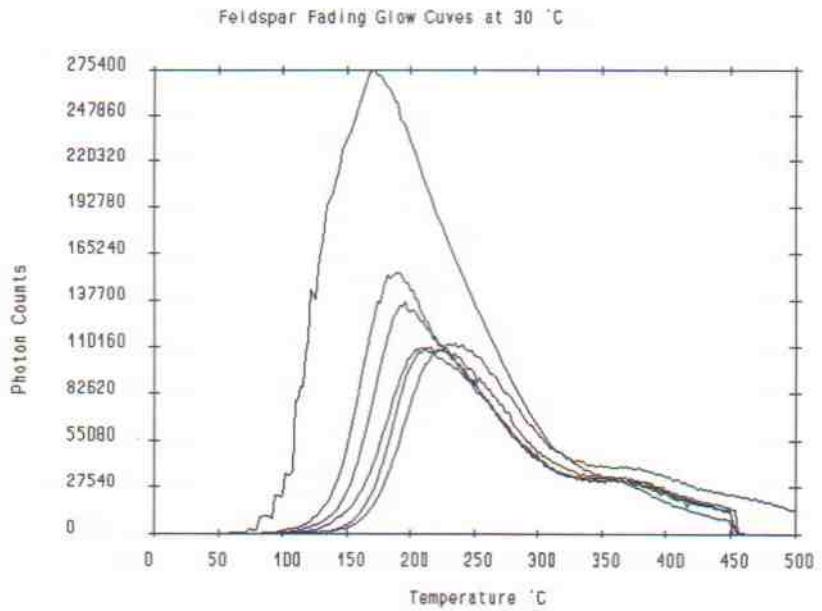

Figure 2.1.3 Standardised glow curves from microcline feldspar stored at 30°C and measured on days 1,3,7,14 and 28. Storage time increases from left to right.

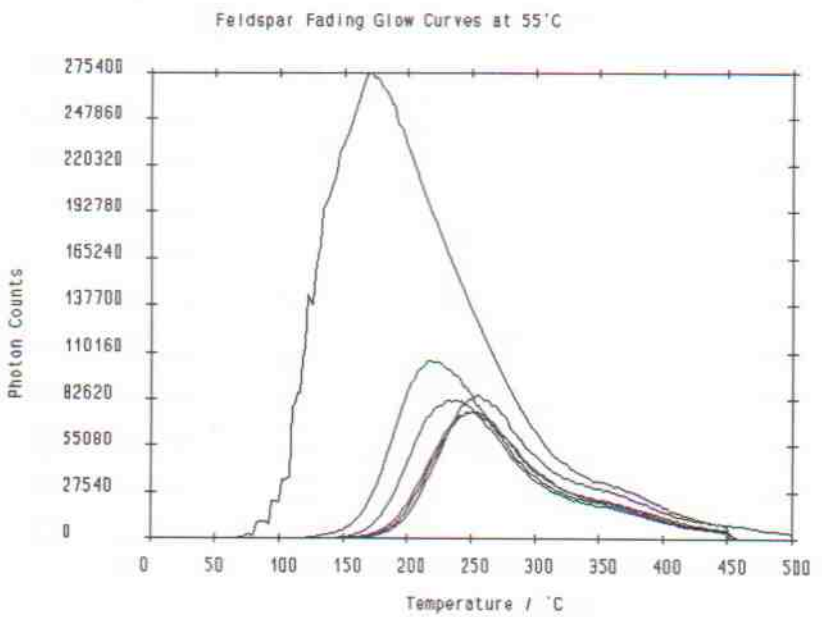

Figure 2.1.4 Standardised glow curves for microcline feldspar stored at 55°C following irradiation. Measurements taken on days 1,3,7,14 and 28 are shown from left to right respectively.

The similarity of glow curve shapes above the initial rise region implies that the trapping distribution is not dominated by low frequency factor components, which would give rise to broad high temperature signals with poor thermal stability. Equally losses throughout the glow curve, due to recombination by tunnelling processes are not a major source of signal loss. The main glow shape changes therefore can be described simply in terms of modification to the initial rise region. This can be parameterised very simply into temperatures corresponding to specified proportions of the intensity change associated with the lowest temperature peak. The temperatures corresponding to 10,50, and 90% of the initial rise intensity were defined at T-10,T-50 and T-90 respectively, and determined using simple glow curve manipulation software. They are shown as a function of storage time and temperature in figures 2.1.5 - 2.1.7. It is notable that the T-50 temperature corresponds to the maximum in the first derivative of the TL glow curve initial rise, and therefore is not only readily determined, but also measured with high temperature precision. Examination of the curves shows that changes to the initial rise follow approximately parallel lines, and in all case show a rapid and readily measured change immediately following irradiation, with much reduced slope at long storage times. It follows from these graphs that the duration of post-irradiation storage can be estimated given knowledge of storage temperatures, and that storage temperature may be estimated providing the duration of exposure is known.

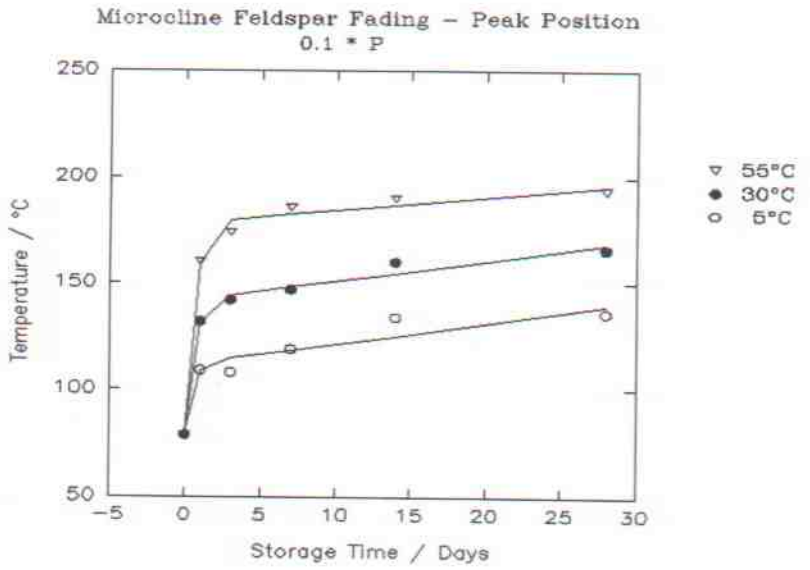

Figure 2.1.5 Variation of T-10% initial rise temperature with storage time and temperature

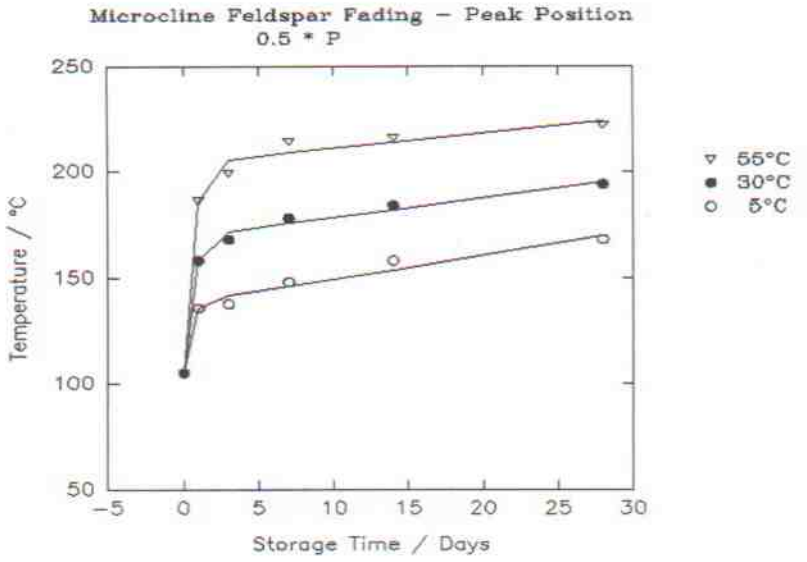

Figure 2.1.6 The variation of T-50% with storage time and temperature

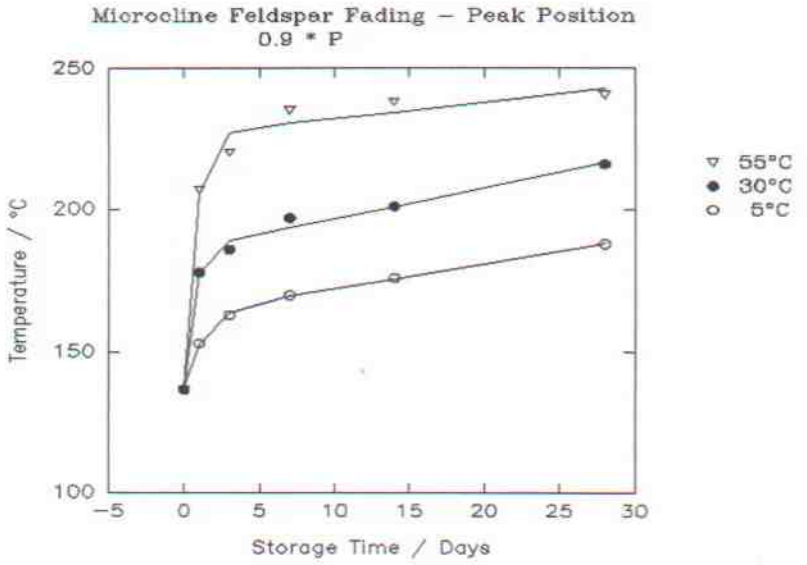

Figure 2.1.7 The variation of T-90% with storage time and temperature

The extent to which individual polymineral sample would need to be calibrated to determine post-irradiation history requires further definition. However there is clearly information in glow curves with a bearing on this question. It is further noted that the disappearance of the

lowest temperature components and a diminishing rate with time, plus the high relative sensitivity of the unstable and metastable low temperature glow curve components has two further implications for detection of irradiated foods. Firstly the glow temperature at which optimal peak to background ratios are obtained, tends to be lower than that for which optimal stability occurs. Therefore consideration of likely storage duration is relevant to the selection and recommendation of which temperature region should be used for routine analysis.

Secondly a more detailed look at glow curve shapes is capable of detecting recent re-irradiation if a previously irradiated product. This is highly significant since re-irradiation is bot prohibited under UK regulations, and recognised as a technological abuse by the Codex Alimentarius commission. A further short model experiment was conducted with pure minerals whereby the glow shape of a sample which had been irradiated twice, separated by a significant delay, was compared with that recorded from a single normalising gamma exposure. As expected the re-irradiated sample showed a pronounced excess peak in the low temperature zone. Simple formation of the spectral ratio of first to second glow TL can identify such anomalies. Again further experiments of a range of irradiated foods would be needed to validate this approach.

2.3 The BCR Interlaboratory study

Although European regulations concerning food irradiation are not currently harmonised, as noted above, the European Commission has been coordinating research into detection methods through a concerted action of the Community Bureau of Reference (BCR). Following meetings and discussions in Brussels and Cadarache in 1990 an interlaboratory trial was proposed to evaluate TL detection methods. At the outset of these discussions there was divided opinion as to whether or not to include whole sample measurements of a randomly selected range of herbs and spices, and the extent to which the study should provide an opportunity for new laboratories to acquire experience of the mineral separation approach. The whole sample method had been recently added to the list of official testing methods in Germany, and was being applied by routine food control laboratories, despite the increasing awareness of it's inherent limitations. In the mean time the SURRC observations of the origins of the TL signals, which had been published and widely circulated in 1989, had been confirmed, firstly in the University of Helsinki (1989), and subsequently in

Karlsruhe, Riso (Denmark) and in Berlin (1990). Once the implications of these findings had been more fully appreciated a decision was finally reached, in March 1991, to focus a short interlaboratory trial on the use of separated minerals, and the need for re-irradiation.

This study was organised at SURRC, jointly with the Berlin Federal Health Office (BGA), and involved 8 laboratories in Denmark, France, Finland, Scotland, Germany, Switzerland and Italy. A further laboratory in Spain had expressed interest but been unable to participate. These laboratories had highly diverse levels of equipment and experience of TL measurements from mineral systems. Three used conventional Harshaw TL dosimetry readers, while the remainder used equipment derived from luminescence research and incorporating photon counting. A set of well characterised reference materials was prepared and circulated to each laboratory to provide a basis for instrumental cross calibration. This included a set of ^{14}C doped low level light sources, obtained from Nuclear Enterprises in Edinburgh and standardised in East Kilbride, and sets of pre-calibrated LiF dosimeters sensitivity matched at SURRC, and irradiated at NPL to four dose levels spanning a range of 10^4. The light sources were intended to serve the dual purposes of cross comparison of detection systems and to to provide each laboratory with an internal stability check during the course of the study. The LiF TLD dosimeters served to cross calibrate both detector linearity, and temperature scales. Each laboratory also received paired samples of 12 commercial grade herbs and spices, either irradiated or unirradiated. The herb and spice samples were procured and irradiated by Dr. Lacroix at IRE in Belgium. Irradiations were accompanied by both 8 Harwell amber perspex dosimeters (routine dosimeters), and a set of 20 NPL alanine ESR dosimeters (reference dosimeters). Both systems were concordant within +-2%.

The laboratories were asked, in addition to instrumental checks, to conduct mineral separations according to a full protocol, and to read the TL signals from first glow, and thereafter following a normalising dose of 1 kGy. Each laboratory was free to arrange the normalising dose in it's own way. Glow curves were integrated into 25°C bands to enable any marked differences in temperature calibration to be taken into account in the analysis.

The results of this study showed that, despite dramatic temperature shifts from laboratory to laboratory (up to 130°C dispersion of the LiF peak 5 temperature estimates), and considerable differences between detector characteristics, it was possible to distinguish the irradiated samples from unirradiated samples with all complete sets of data, when the full second glow normalisation procedure was used. Unnormalised data were not able to discriminate between all samples used in this study.

Two laboratories were unable to complete the study for instrumental reasons; one was unable to integrate glow curves, the other unable to re-irradiate to 1 kGy. There was clear evidence of cross contamination in some un-normalised data sets, particularly from laboratories with no prior experience. However even in these cases the normalised results were still able to separate the irradiated and unirradiated samples.

A copy of the draft report on this study is appended to this report, in appendix D. It was remarkable given the diverse experience and equipment of the participating laboratories that the full procedure was sufficiently robust to yield concordant results.

2.4 The MAFF Non-Statutory Validated Method

Following the confirmation of SURRC findings concerning the origins of TL signals from herbs and spices, and the demonstration through the BCR study, that the procedures could be adopted successfully by other laboratories, a formal protocol was prepared for UK use to define a recognised test procedure. This document was published in 1992 as V.27 in the MAFF Non-Statutory Validated Methods series, and represents the first formally recognised detection method for irradiated food, which can now be used for enforcement of UK regulations. A similar protocol has been submitted to BCR, and may serve as the basis for an international standard method.

The full procedure is presented in appendix E. In addition to full step by step instructions for the laboratory procedures, a set of quality assurance steps have been defined, and examples given of the classification criteria for irradiated samples. The procedure uses full mineral separation and radiation normalisation. Quality assurance measures include rigorous checks

on glassware and reagent blanks, definition of instrumental minimum detection levels and limits of saturation, duplex analysis of separate aliquots and a formal check for concordance. Any result for which the response after re-irradiation is below 10 times minimum detectable level is rejected.

This procedure appears to be robust, and is already being used to a limited extent in support of the UK regulations.

2.5 Proposed procedures for fruits and vegetables

Having established a validated method for herbs and spices, the next natural progression of the project was to supplement the range and types of samples, to which TL methods could be applied. Exotic fruits and imported vegetables are candidates for radiation preservation since they are high value products, easily perishable, and can benefit from shelf life extension by radiation processing. Some of these products originate in countries with irradiation facilities, while others are traded internationally through countries with active irradiation programmes. Although Codex Alimentarius standards are widely accepted, it is not clear to what extent international standards for food irradiation conform to UK regulations.

All fruits and vegetables will have been exposed to environmental conditions which will cause mineral debris to be deposited on the surface. To exploit this it remains to demonstrate that such material can be recovered from a wide selection of product types, and to establish the extent to which TL signals derived from such material can be used to identify irradiated samples. Chapter 3 presents results from work on the extraction of minerals from the surfaces of fruits and vegetables, while Chapter 4 examines the stability of TL signals from Mangos under illuminated storage.

3 Extension of separation to fruits and vegetables

3.1 Initial survey of TL response from vegetables

Initial experimentation was carried out on potato samples using a simplistic approach. The sample was ultra-sonically shaken in deionised water for 30 minutes to remove adhering grains. The sample removed and the solution left to settle. The water layer was decanted off and the remaining mineral suspension washed several times with water. The minerals were the resuspended in acetone and displaced on stainless steel discs. The results proved promising. This technique was used on a selection of twenty vegetables samples shown in table 3.1, purchased from various local outlets. The whole samples were split , one portion was used as a control and the other given a 1 kGy dose in the Cobalt-60 source. The separation to both control and irradiated samples was carried out in duplex parallel extraction and all operations were carried out under safe light conditions. The discs were readout on the SURRC TL reader and a normalisation dose of 1kGy was then given to the discs and the ratios of the first glow to the second glow were taken.

The glow curves for the vegetable samples are shown in figures 3.1.1 - 3.1.20. These curves were integrated and used to plot standard glow ratio histograms (figure 3.1.21), first vs second glow plots (figure 3.1.22) and concordance diagrams for paired replicates (figure 3.1.23). The plot of first glow versus second (renormalisation) glow for the irradiated and unirradiated vegetables.

The vegetable samples fall into two distinct loci which do separate irradiated and unirradiated samples.

Table 3.1 : Vegetable Samples

Filename	Samples
SP394	New Potatoes
SP395	Parsnips
SP396	Mushrooms
SP397	Brocoli
SP398	Onions
SP399	Aubergine
SP400	Green Pepper
SP401	Red Pepper
SP402	Beans
SP403	Okra
SP404	Mange-tout
SP405	Celery
SP406	Carrots
SP407	Leek
SP408	Sweet Potatoes
SP409	Cauliflower
SP410	Garlic
SP411	Courgettes
SP412	Brussel Sprouts
SP413	Eddoes

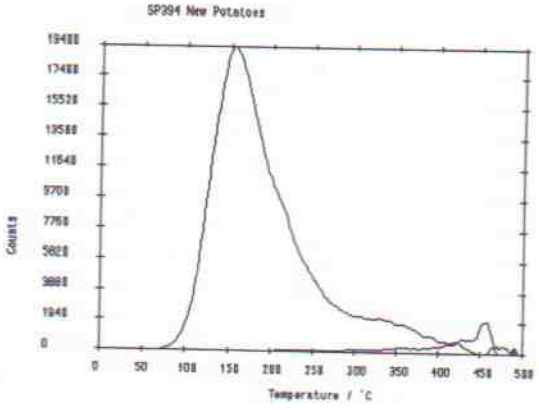

Figure 3.1.1 Irradiated and Control Glow Curves for New Potatoes

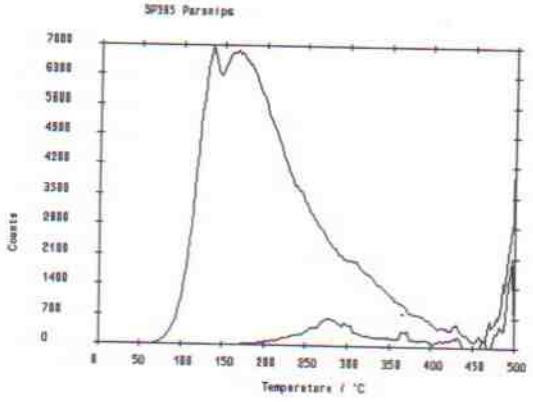

Figure 3.1.2 Irradiated and Control Glow Curves for Parsnips

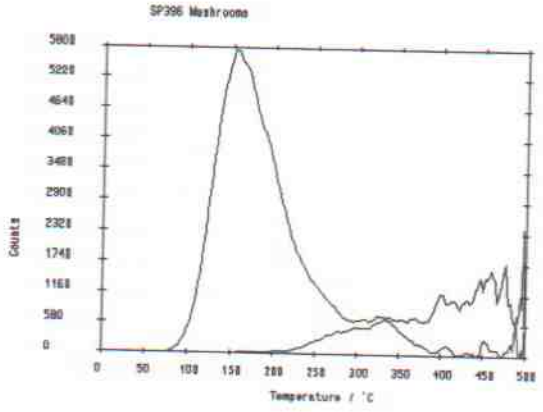

Figure 3.1.3 Irradiated and Control Glow Curves for Mushrooms

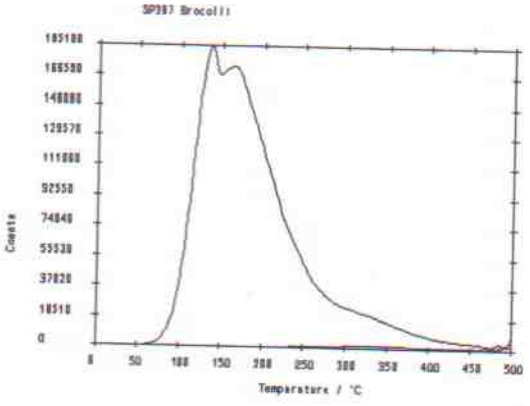

Figure 3.1.4 Irradiated and Control Glow Curves for Broccoli

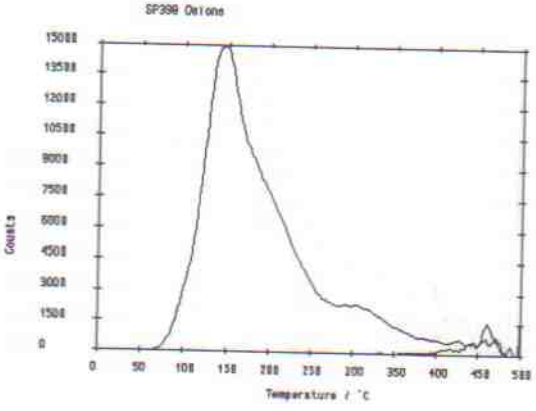

Figure 3.1.5 Irradiated and Control Glow Curves for Onions

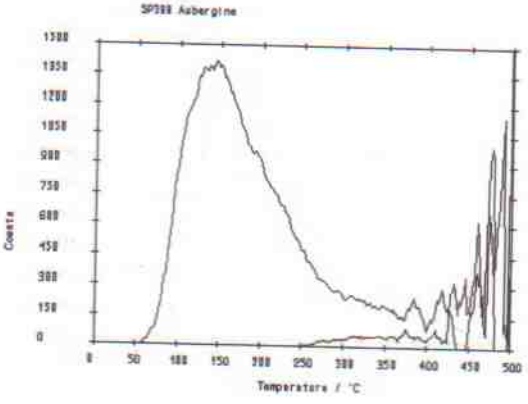

Figure 3.1.6 Irradiated and Control Glow Curves for Aubergines

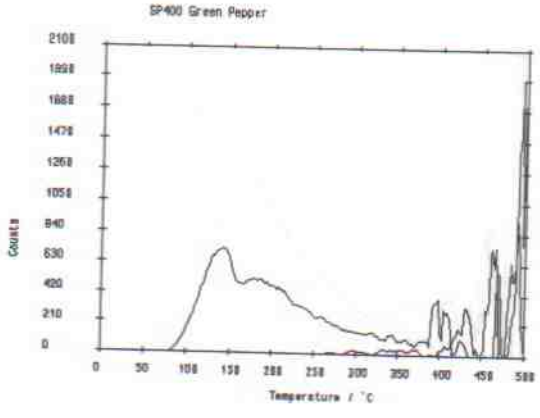

Figure 3.1.7 Irradiated and Control Glow Curves for Green Peppers

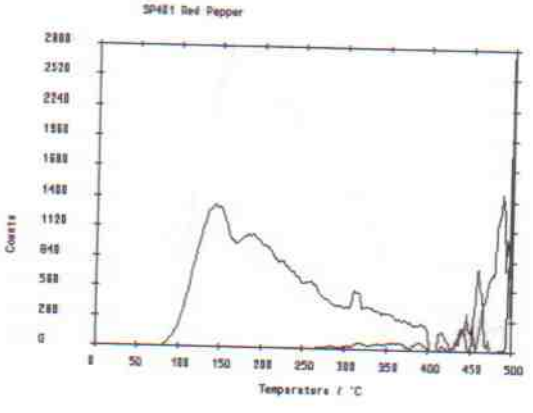

Figure 3.1.8 Irradiated and Control Glow Curves for Red Peppers

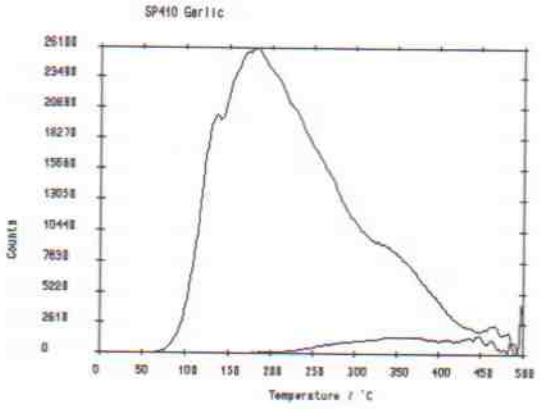

Figure 3.1.17 Irradiated and Control Glow Curves for Garlic

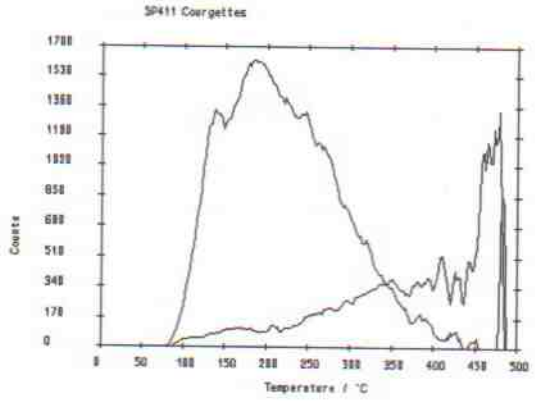

Figure 3.1.18 Irradiated and Control Glow Curves for Courgettes

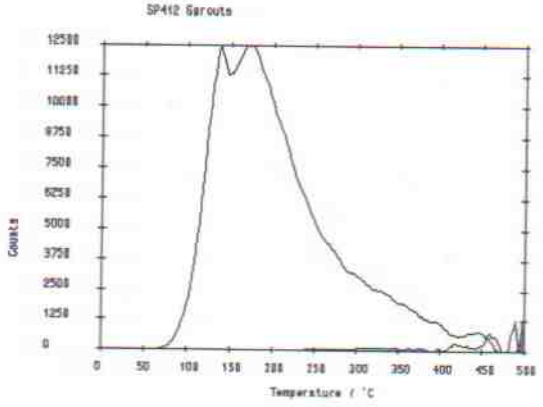

Figure 3.1.19 Irradiated and Control Glow Curves for Sprouts

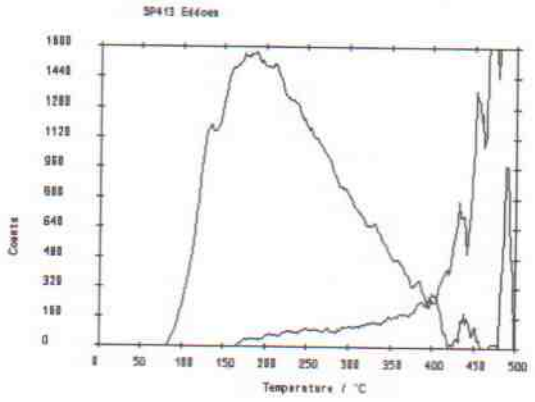

Figure 3.1.20 Irradiated and Control Glow Curves for Eddoes

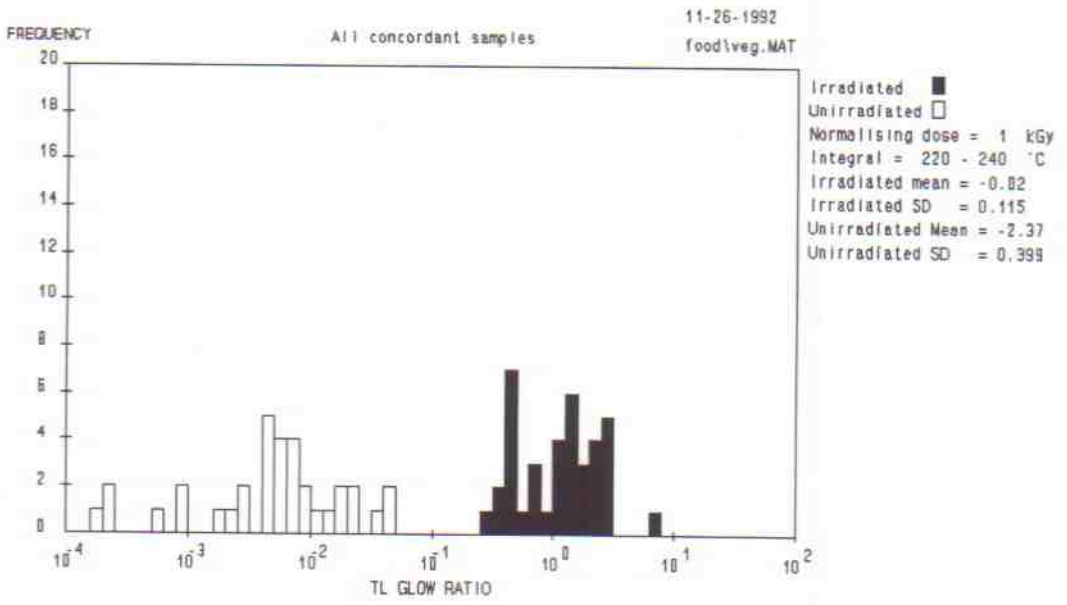

Figure 3.1.21 Glow Ratio Histogram for Vegetable Samples

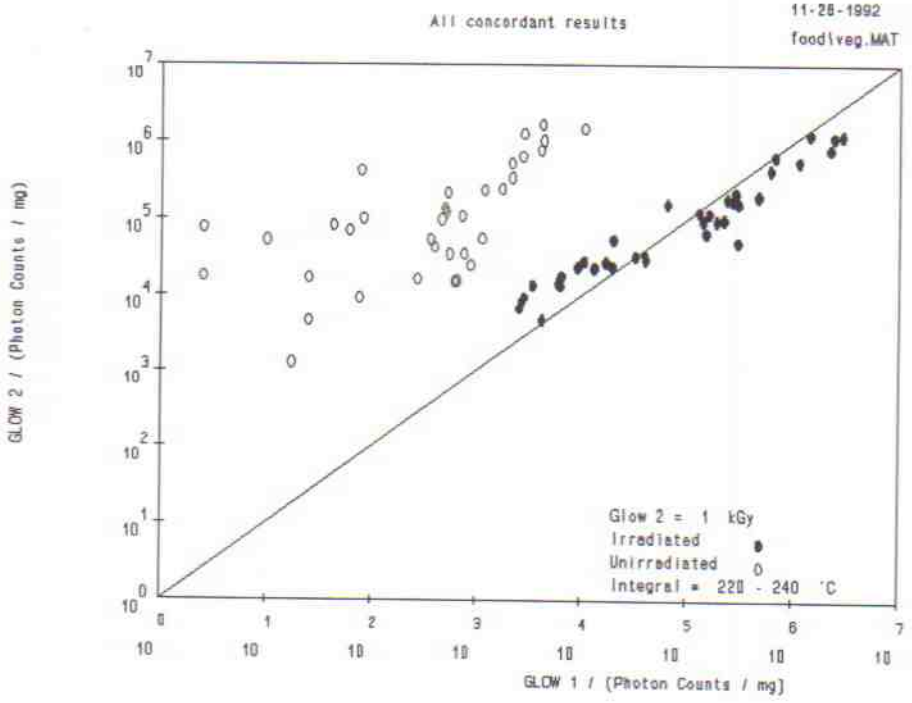

Figure 3.1.22 First vs Second Glow Plot for Vegetable Samples

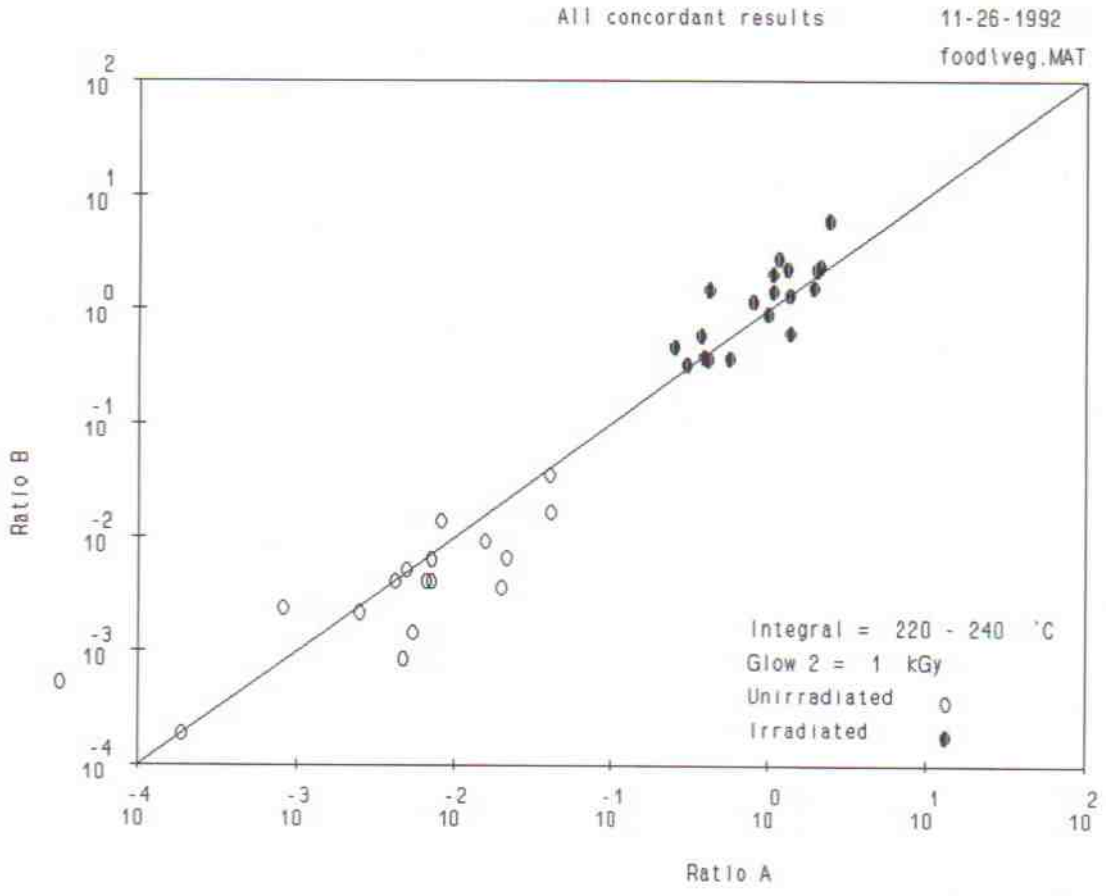

Figure 3.1.23 Concordance Diagram for Paired Replicate Vegetable Samples

3.2 Initial survey of TL response from fruits

The separation of vegetable samples gave very promising results with good discrepancies between irradiated and unirradiated samples, so this simple method was applied to twenty-two fruit samples, shown in Table 3.2. The whole samples were split and one portion was given a 1kGy dose in the Cobalt-60 source and the other used as a control. The irradiated samples and blanks were both subject to duplex parallel extraction, with all operations carried out under safe light conditions. To prevent contamination from the atmosphere each beaker containing the fruit sample dispersed in de-ionised water was covered with cling film and shaken in the ultrasonic bath for 30 minutes. After shaking, the contents were left to settle for 2 hours. The samples were removed, dried and placed in resealable bags for storage. The liquids were decanted into a large centrifuge tube and centrifuged down. This continued until all the liquids were centrifuged down. The samples were then washed several times with deionised water. The minerals were suspended in acetone for 10 minutes and this step was repeated to remove all traces of water. A small amount of acetone was added and the samples dispensed into settling tubes containing stainless steel discs and the acetone dried off overnight in an oven at 55°C. The discs were readout on the SURRC TL reader and a normalisation dose of 1kGy was then given to the discs. Then the ratios of the first glow to the second glow were taken.

Table 3.2 : Fruit Sample

Filename	Sample
SP360	Pomegranite
SP361	Red Plums
SP362	Cox's Apples
SP363	Pears
SP364	Mangos
SP365	Oranges
SP366	Kiwi Fruit
SP367	Black Grapes
SP368	Passion Fruit
SP369	Tomatoes
SP370	Clementines
SP371	Guavas
SP372	Sharon Fruit
SP373	Prickely Pears
SP374	Grenadillo
SP375	Paw Paw
SP376	Lemons
SP377	Carambda
SP378	Limes
SP379	Strawberries
SP380	Pineapples
SP381	Dates

A selection of glow curves for fruits are shown in figures 3.2.1 - 3.2.22.

The histograms of first glow to second glow for the separated minerals for fruits are shown in figure 3.2.23. Figure 3.2.24 shows the two dimensional plot of first glows versus second (renormalisation) glow for the results for irradiated and unirradiated samples. Confirming that sensitivity variations are significant. Figure 3.2.25 shows the concordance plots for fruits.

The results clearly show that it is possible to separate minerals from fruits. Separation of minerals from some samples was incomplete and can be seen especially in the case of the fruit samples. Microscopic examination of the minerals on discs in fruit revealed great variation in the number of grains on each disc and also the presence of a residue. The TL sensitivity of the mineral grains was highly variable for the samples.

The results from the histogram, glow1 versus glow2 ratio and concordance plots of the fruit samples, show that their properties range over several orders of magnitude, resulting in blank samples lying amongst the irradiated. This overlay is most probably caused by spurious TL from slight residue on many of the discs, instead of cross-contamination from glassware, reagents or air borne particles due to stringent laboratory quality control. Hence further investigation and development of the separation method on fruit samples.

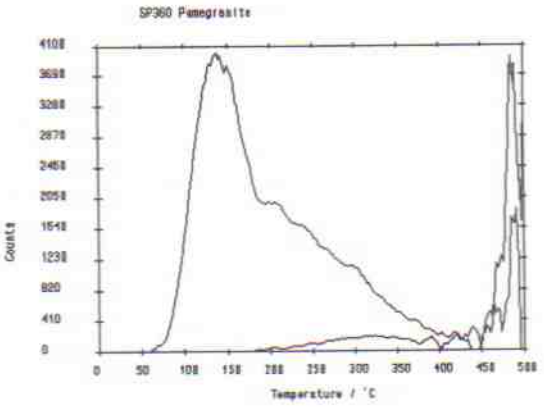

Figure 3.2.1 Irradiated and Control Glow Curves for Pomegranites

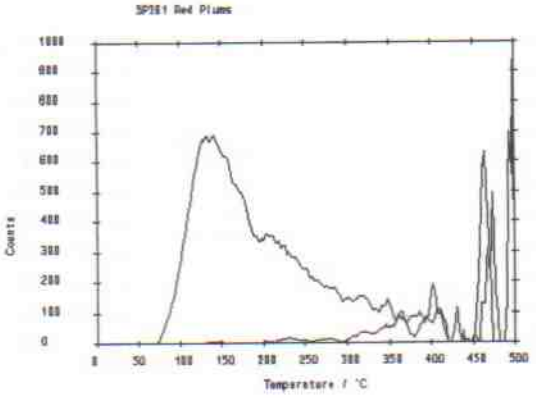

Figure 3.2.2 Irradiated and Control Glow Curves for Red Plums

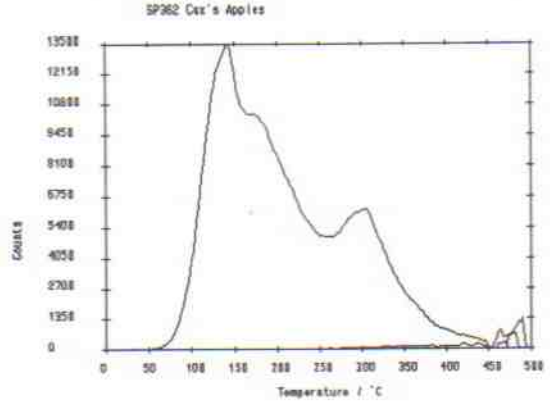

Figure 3.2.3 Irradiated and Control GLow Curves for Cox's Apples

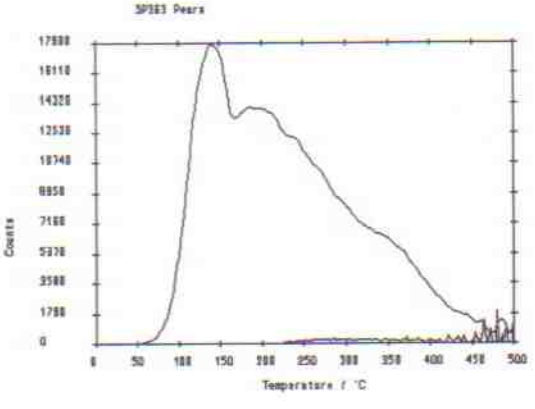

Figure 3.2.4 Irradiated and Control Glow Curves for Pears

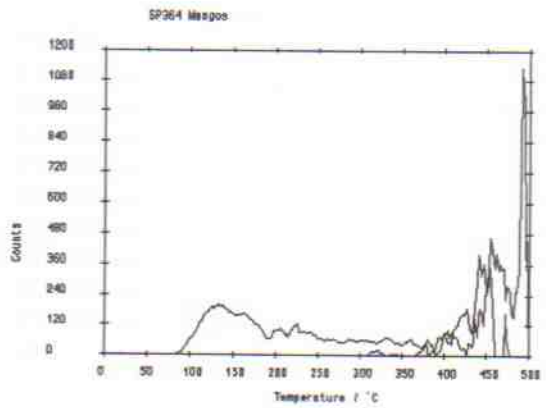

Figure 3.2.5 Irradiated and Control Glow Curves for Mangos

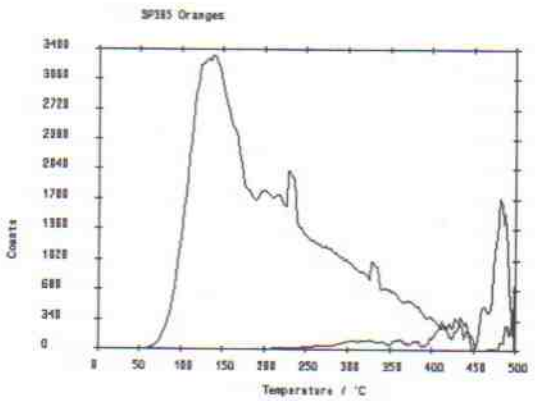

Figure 3.2.6 Irradiated and Control Glow Curves for Oranges

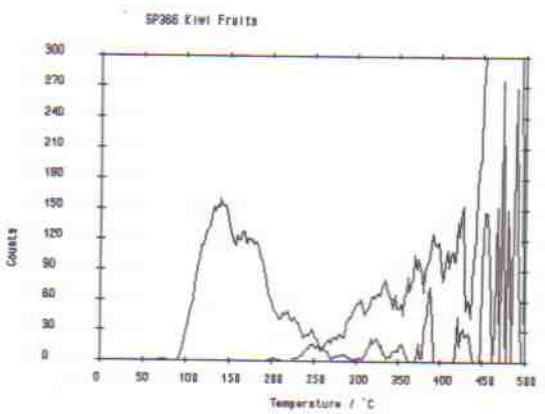

Figure 3.2.7 Irradiated and Control Glow Curves for Kiwi Fruits

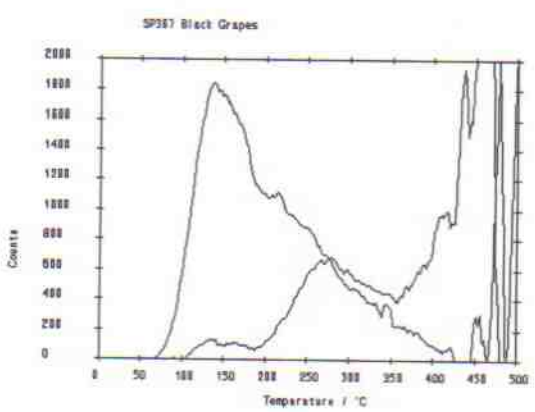

Figure 3.2.8 Irradiated and Control Glow Curves for Black Grapes

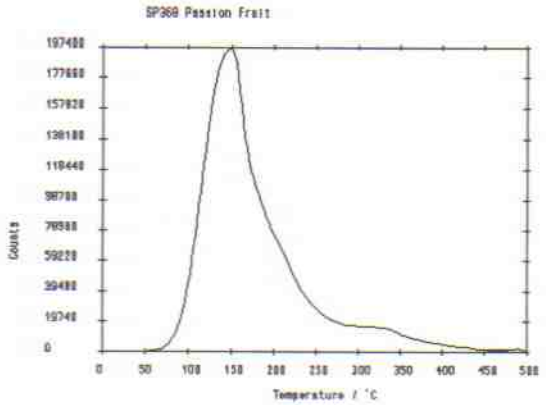

Figure 3.2.9 Irradiated and Control Glow Curves for Passion Fruits

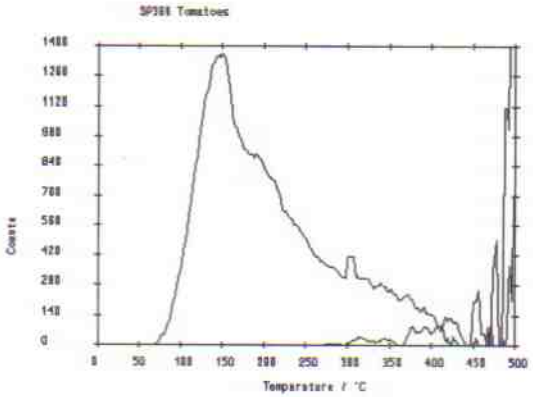

Figure 3.2.10 Irradiated and Control Glow Curves for Tomatoes

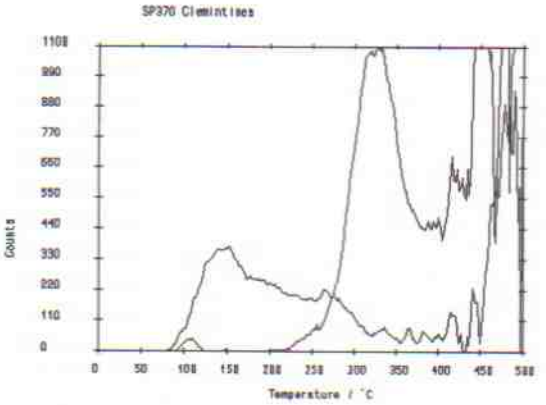

Figure 3.2.11 Irradiated and Control Glow Curves for Clemintines

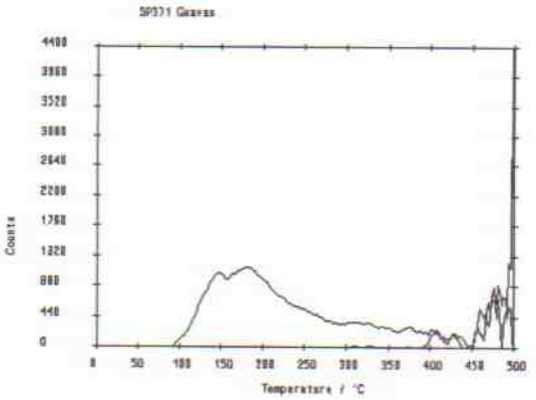

Figure 3.2.12 Irradiated and Control Glow Curves for Guavas

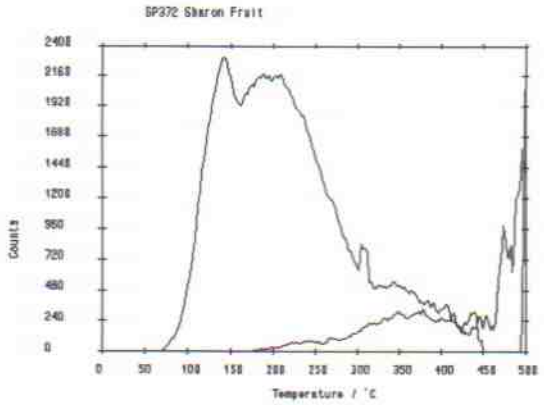

Figure 3.2.13 Irradiated and Control Glow Curves for Sharon Fruit

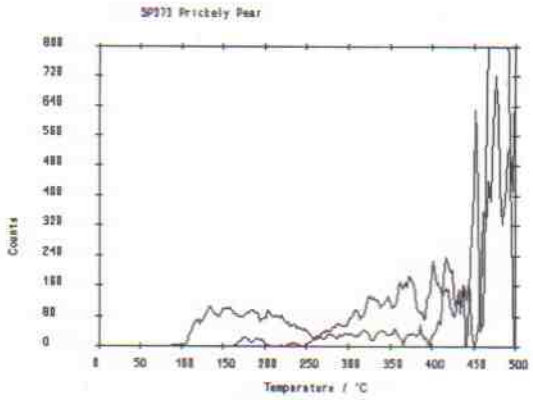

Figure 3.2.14 Irradiated and Control Glow Curves for Prickely Pears

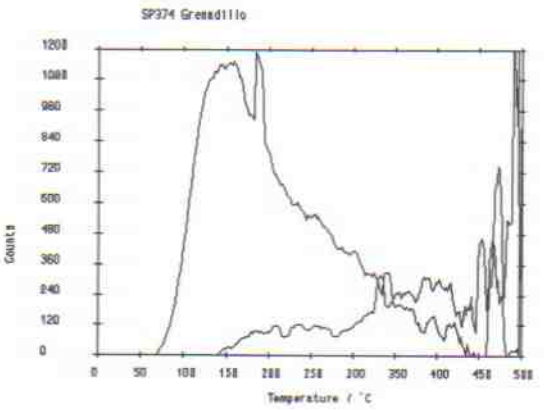

Figure 3.2.15 Irradiated and Control Glow Curves for Grenadillos

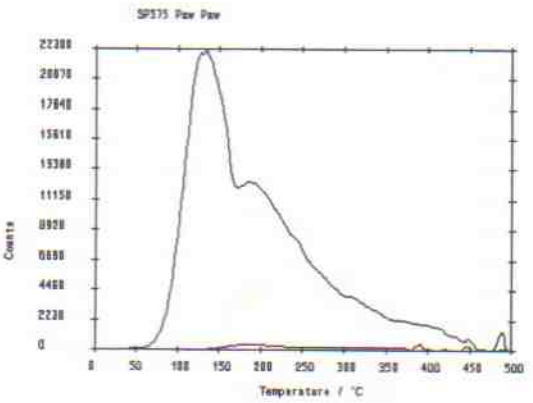

Figure 3.2.16 Irradiated and Control Glow Curves for Paw Paw's

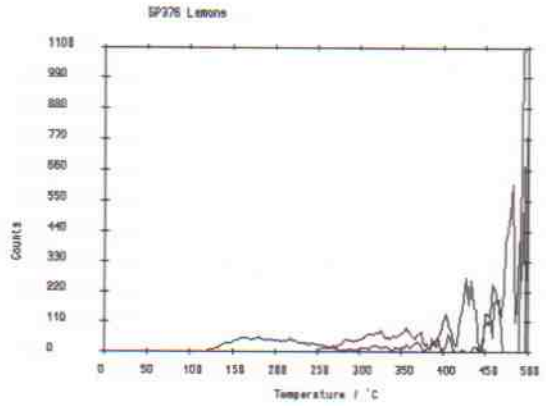

Figure 3.2.17 Irradiated and Control Glow Curves for Lemons

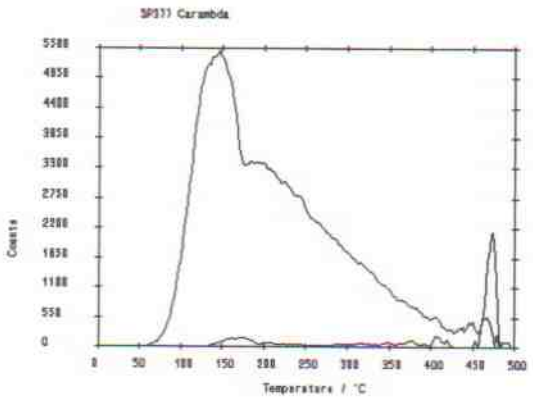

Figure 3.2.18 Irradiated and Control Glow Curves for Carambda's

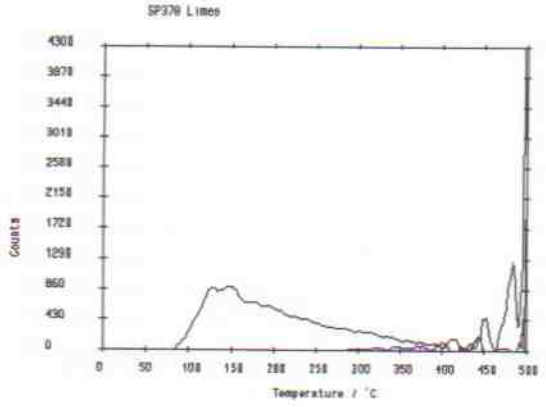

Figure 3.2.19 Irradiated and Control Glow Curves for Limes

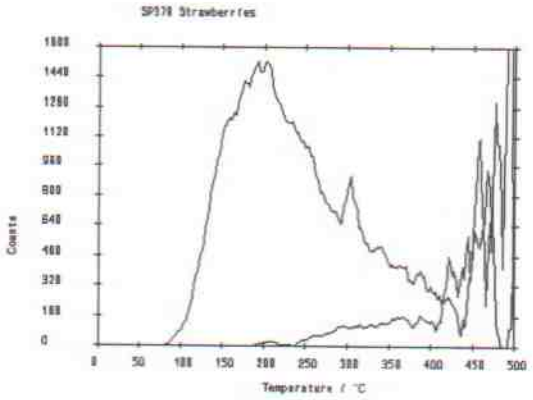

Figure 3.2.20 Irradiated and Control Glow Curves for Strawberries

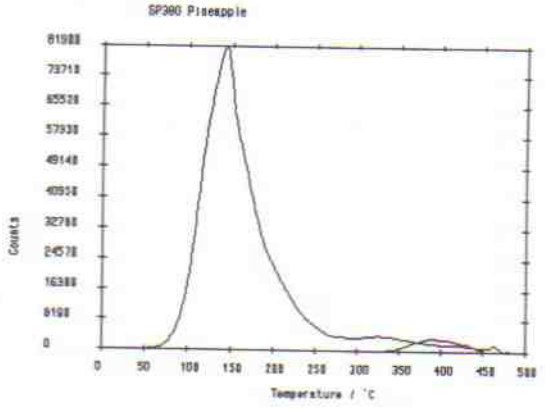

Figure 3.2.21 Irradiated and Control Glow Curves for Pineapples

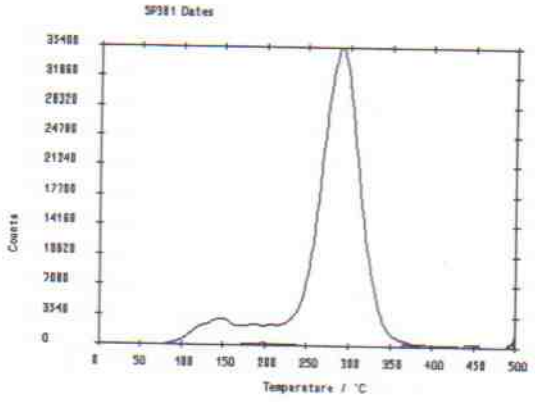

Figure 3.2.22 Irradiated and Control Glow Curves for Dates

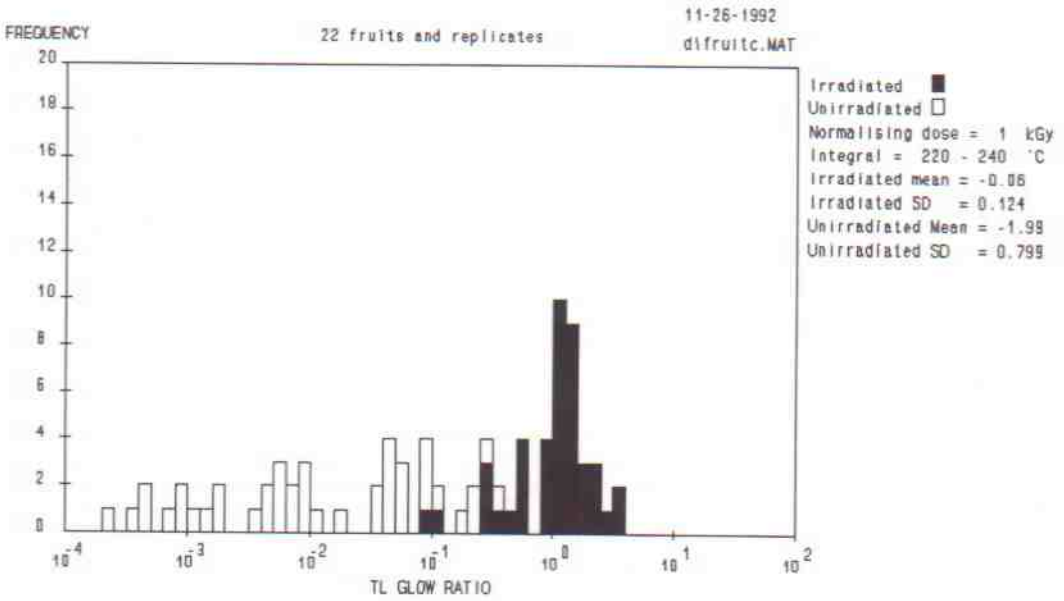

Figure 3.2.23 Glow Ratio Histogram for the Water Separated Minerals of Fruits

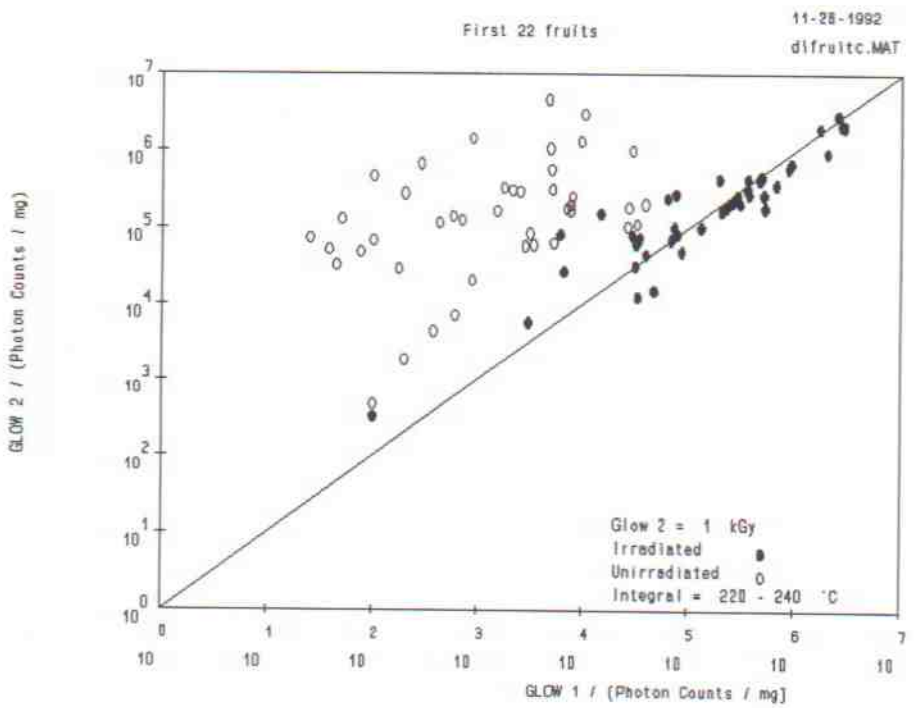

Figure 3.2.24 Glow 1 vs Glow 2 Ratio Plots for Water Separated Minerals of Fruits

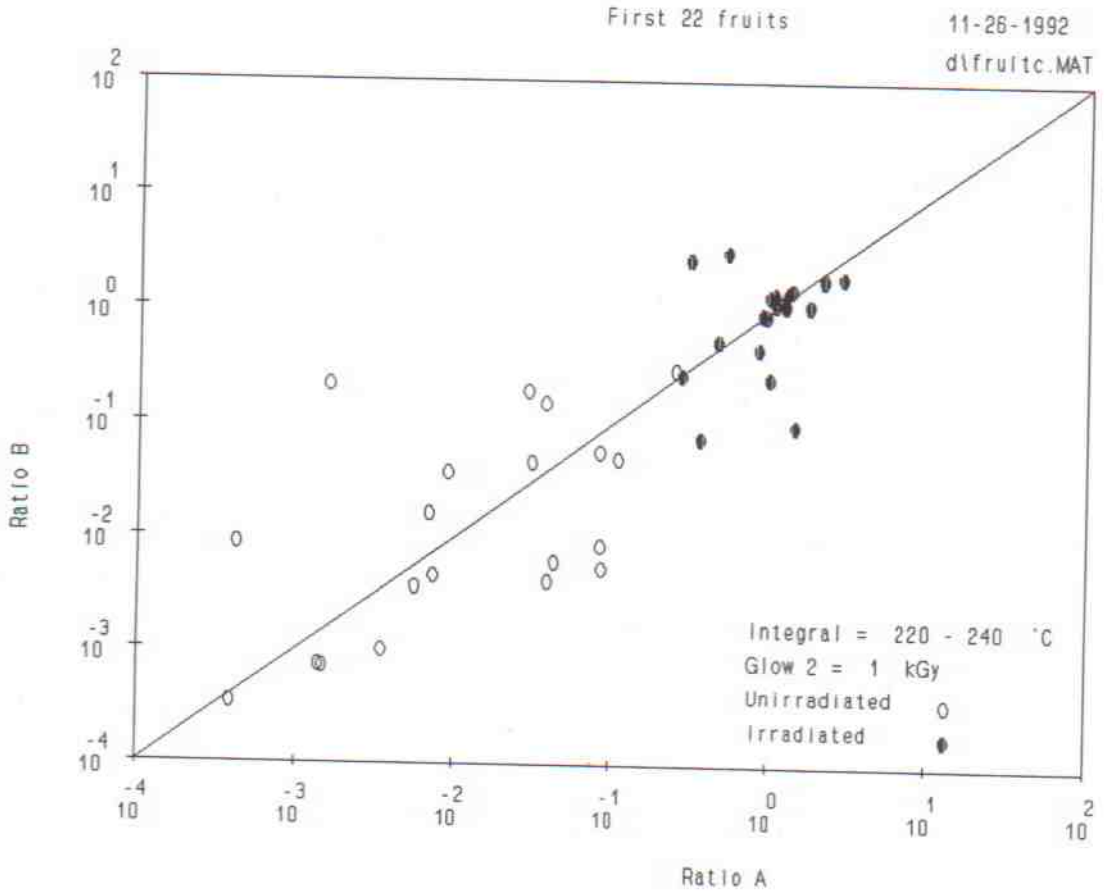

Figure 3.2.25 Concordance Plot Of Water Separated Minerals of Fruits

3.3 Improved procedure for fruits

A further set of twelve fruits were purchased as shown in Table 3.3. Stringent precautions were taken to prevent cross-contamination from the air, glassware, reagents and loss of mineral grains from the discs during the renormalisation step.

From our initial experiments with the fruit samples the results have shown that it is possible to remove mineral grains, however the simple water extraction method is not sufficient in the fruits. The poor discrimination could be the presence of carbonates, or from the presence of a "waxy" coating on some of the fruits, apparantly used to enhance the appearance of the fruit and in some cases used as a protective layer from damage.
Further experimentation was then carried out using the water extraction method as a pre-concentration step and then the full density separation technique as used for herbs and spices.

Strawberries and soft fruits proved to be very difficult to separate, forming either a gel or high density phase during the tungstate stage. This problem of the minerals "encapsulated" in this gelatinous phase can be resolved by several washings and ultrasonic shakings with deionised water. The upper layer is then decanted off and the minerals are suspended in 1M hydrochloric acid and shaken for 15 mins in an ultrasonic bath.

The glow curves for the fruit samples are shown in figures 3.3.1 - 3.3.12 and the results, shown in figures 3.3.13, 3.3.14 and 3.3.15 show a dramatic improvement in discriminating and identification of irradiated and unirradiated samples.

Table 3.3 : Fruit Samples

Filename	Sample
SP382	Sharon Fruit
SP383	Kiwi Fruit
SP384	Grenadillo
SP385	Star Fruit
SP386	Jaffa Sweetie
SP387	Plums
SP388	Kiwi Fruit
SP389	Sharon Fruit
SP390	Star Fruit
SP391	Lychees
SP392	Mangos
SP393	Paw Paw

Figure 3.3.1 Irradiated and Control Glow Curves for Sharon Fruits

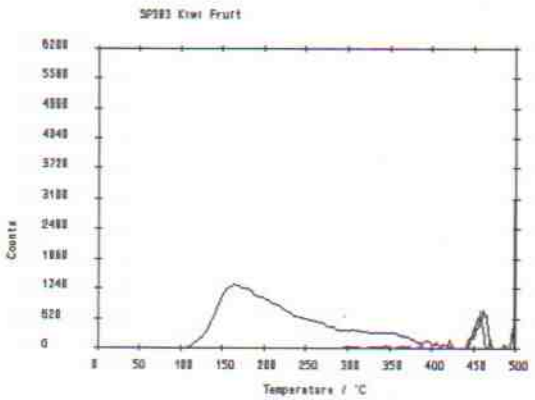

Figure 3.3.2 Irradiated and Control Glow Curves for Kiwi Fruits

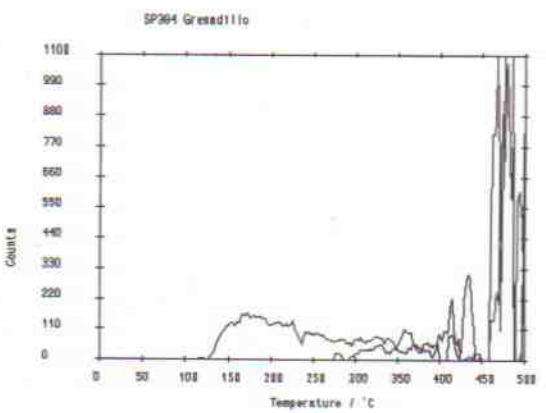

Figure 3.3.3 Irradiated and Control Glow Curves for Grenadillo's

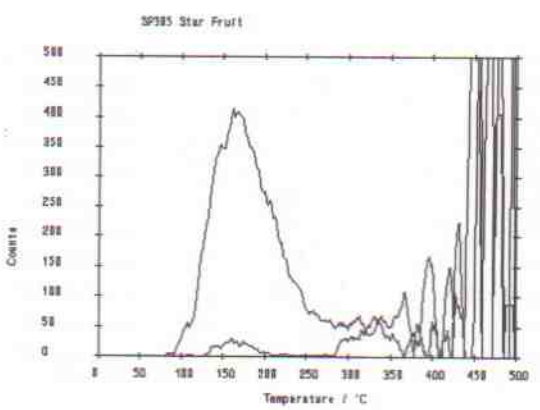

Figure 3.3.4 Irradiated and Control Glow Curves for Star Fruits

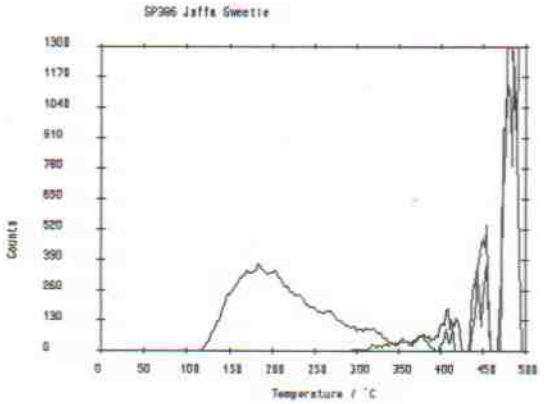

Figure 3.3.5 Irradiated and Control Glow Curves for Jaffa Sweeties

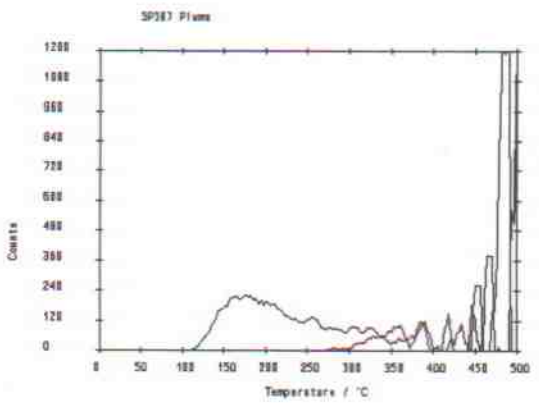

Figure 3.3.6 Irradiated and Control Glow Curves for Red Plums

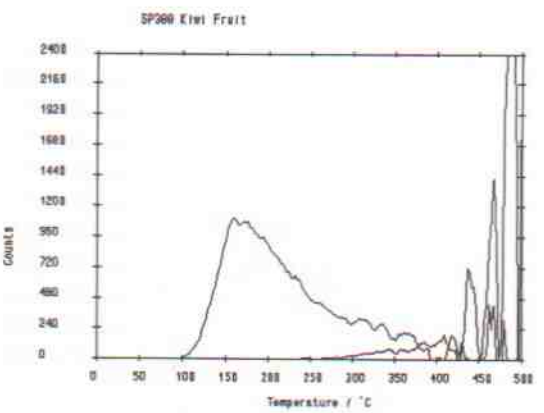

Figure 3.3.7 Irradiated and Control Glow Curves for Kiwi Fruits

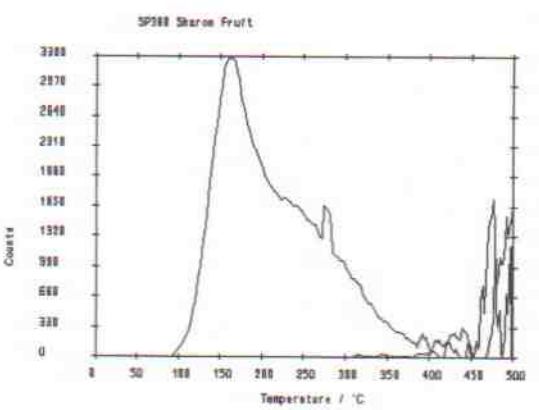

Figure 3.3.8 Irradiated and Control Glow Curves for Sharon Fruits

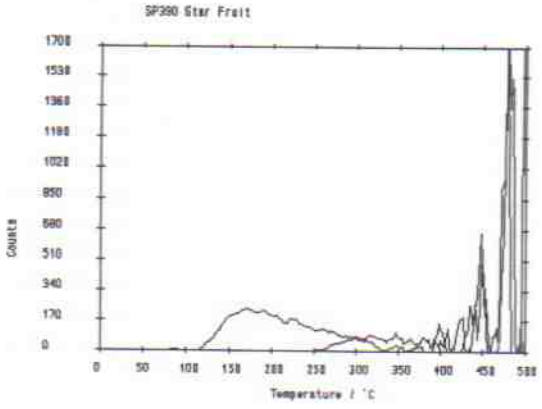

Figure 3.3.9 Irradiated and Control Glow Curves for Star Fruits

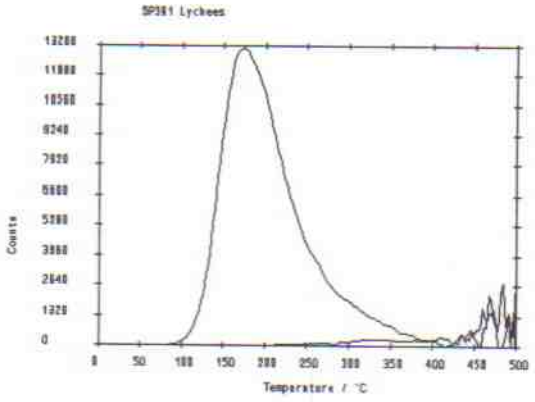

Figure 3.3.10 Irradiated and Control Glow Curves for Lychees

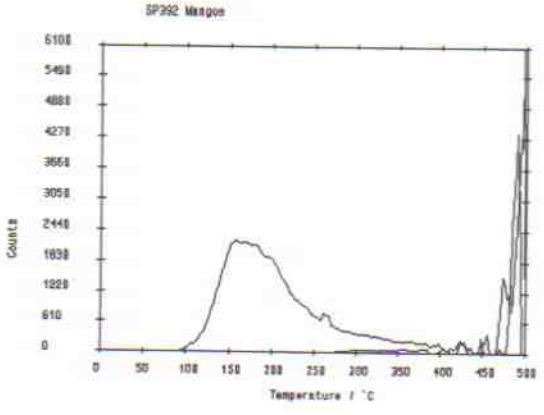

Figure 3.3.11 Irradiated and Control Glow Curves for Mangos

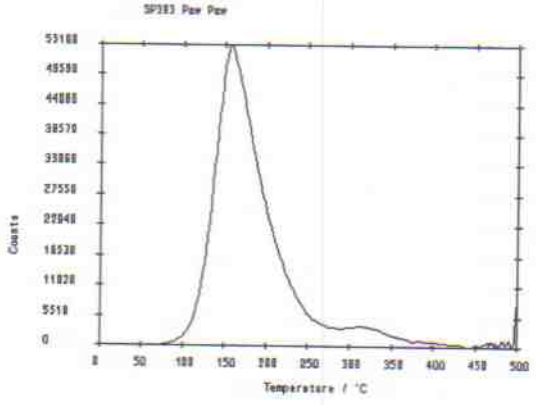

Figure 3.3.12 Irradiated and Control Glow Curves for Paw Paw's

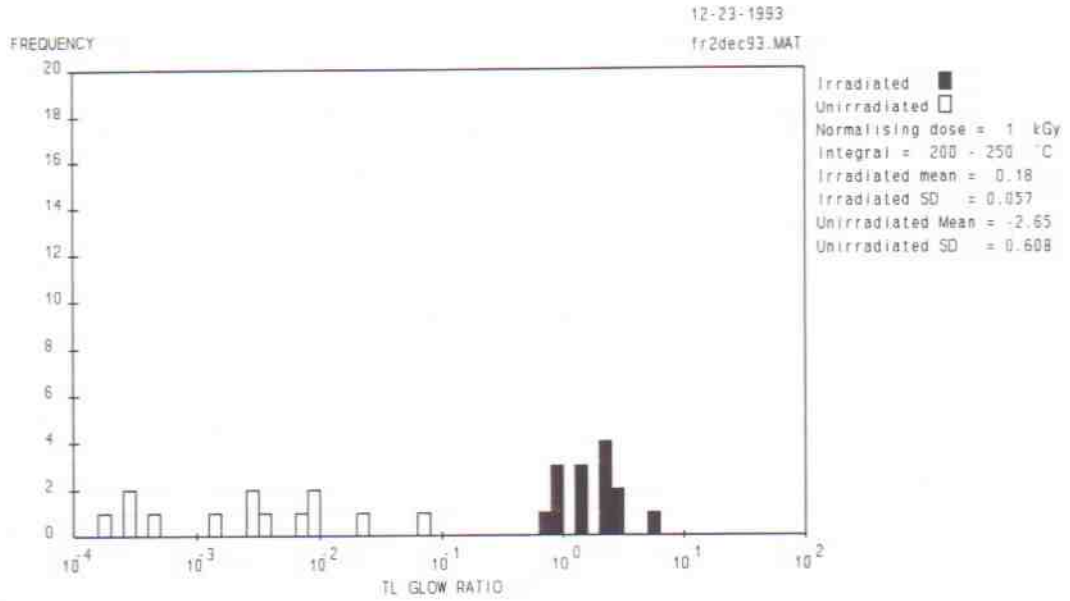

Figure 3.3.13 Glow Ratio histogram of separated minerals from fruits. Samples whose second glow TL was below 10xMDL, or which failed concordance checks were omitted.

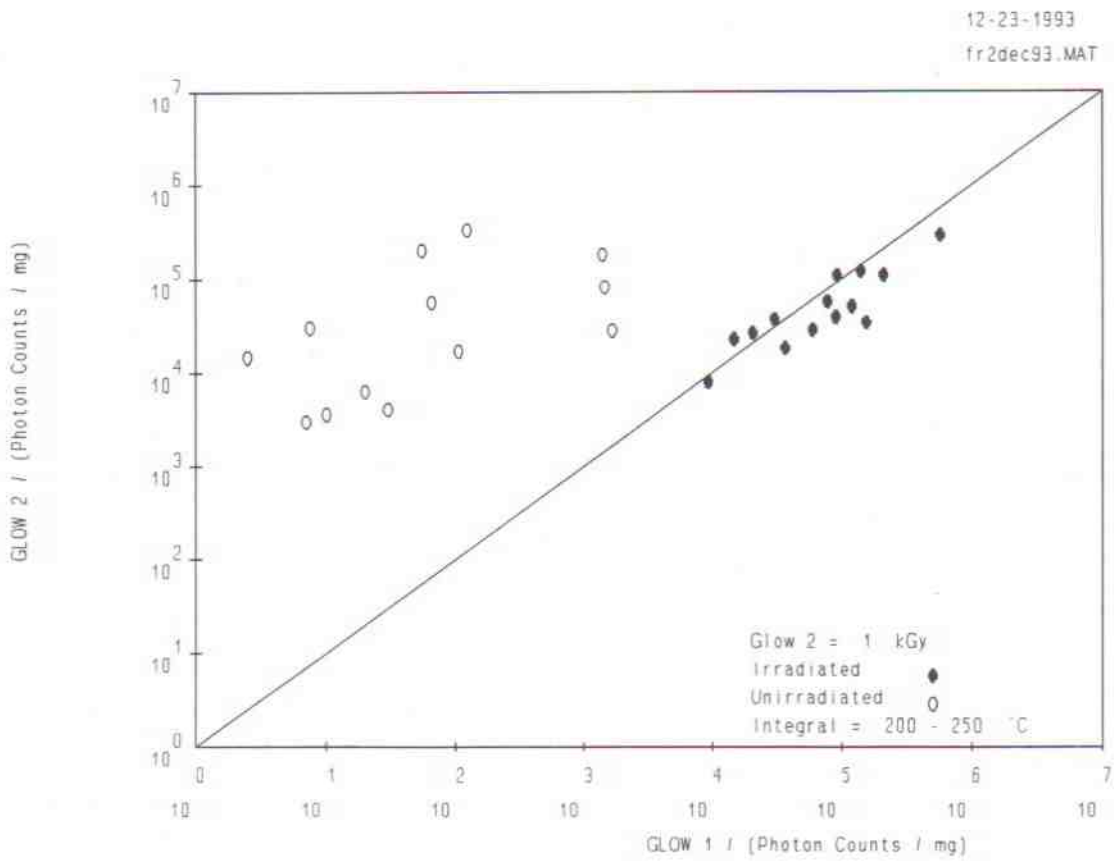

Figure 3.3.14 First vs Second Glow Plot for Density separated minerals from fruit.

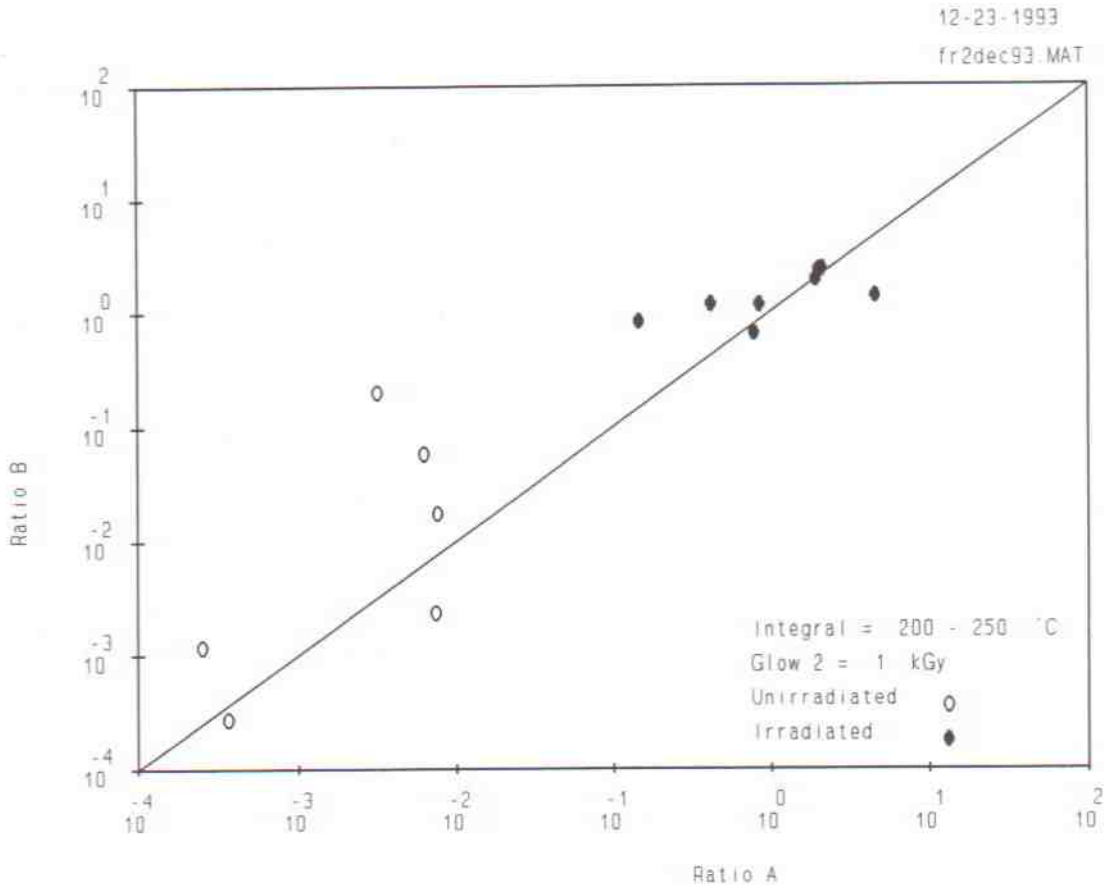

Figure 3.3.15 Concordance plot for separated minerals from replicated fruits.

3.4 Discussion

Initial surveys confirmed the ability to extract minerals from fruits and vegetables. In fruits, especially soft fruits, a thin film of organic residue was deposited along with the minerals on the disc with a simple water extraction. The organic residue can be removed by extrusion of the sample handling to include the density separation stage and prolonged HCl acid clean up.

Vegetables gave good results providing that concordance checks were made and good quality assurance procedures used to identify suspect results.

Good discrimination can be achieved between irradiated and unirradiated samples, providing that diligent sample handling, good quality assurance and quality control. The implementation of the full density separation technique, the use of glow ratio histograms, first / second glow plots and concordance diagrams is necessary.

4. Post Irradiation stability of thermoluminescence under illumination

4.1 Optical Bleaching

It has been shown that it is possible to successfully separate minerals from fruits and vegetables and distinguish irradiated samples from unirradiated. Supermarkets and greengrocers normally display fruits and vegetables under strong lights to make the items more appealing to the customer. Certain areas of the TL signal are known to be susceptible to optical bleaching. This effect may significantly reduce the sensitivity of the TL signal from separated minerals of fruits and vegetables, resulting in the indistinguishability of irradiated and unirradiated samples. Clearly fruits and vegetables are more vulnerable to optical bleaching than other types of food, and therefore a set of illumination experiments was planned to evaluate the extent to which this could effect qualitative idetification of irradiated fruits.

In order to ascertain the effect that optical bleaching may have on the shape and intensity of the glow curves from fruits and vegetables during handling two experimental light-boxes were set to simulate this effect under controlled conditions.

The choice of design and methods for characterisation were reached after consultation with NPL and the research section of Thorn-Emi lighting. It was apparent that fluorescent lighting was the most suitable source to represent illumination in retail conditions, and Thorn lighting recommended two tube types : Artificial daylight and Natural deluxe. Both types are widely used in supermarkets ; both present spectra with continuum and line components, the former having an equivalent colour temperature appropriate to mean daylight in the northern hemisphere, the latter having less UV/blue components and a warmer overall effect. Natural deluxe is widely used in retail outlets as it gives a succulent appearance to meats, and a fresh colourful look to fruits.

4.2 Construction of Lightboxes for Bleaching Tests

Two lightboxes were built from thick PVC to the dimensions of 150cm x 60cm x 56cm, with a small but resealable flap, for sample handling. Samples in the shops could be subjected to weeks of optical bleaching and to reduce the simulation time to hours rather than days four

tubes were installed into the lightboxes, and the samples placed in close proximity to the illumination.

A set of silicon photodiodes was used both for mapping the distribution of illumination within the lightboxes (see below) and also to provide continuous quality control monitoring during bleaching experiments. A control box was constructed containing low noise amplifiers and four channel comparators set up to provide a continuous display of the mean intensity, and an immediate indication if any one of the four tubes failed. Absolute calibrations of the energy fluence within the boxes was achieved using a Molectron PR500 pyroelectric radiometer with integral optical chopper.

Extensive laboratory experiments were carried out to standardise the intensities the tubes and to obtain the most even spread of the light within the boxes. These are described below.

4.2.1 Lightbox Setup

Four experiments were undertaken to map the distribution of light within the sample plane, rearranging the tubes and adding temporary paper reflectors at each stage. It was clearly established that the addition of reflectors improved uniformity, and therefore the interior surfaces of the boxes were painted with TiO_2 reflective paint (from Nuclear Enterprises) to make a permanent arrangement before absolute measurements of energy fluence were undertaken. Intermediate results of the intensity mapping experiments are presented below.
Experiment 1: Each lightbox contained four tubes with no reflectors. A X/Y-grid was draw on the base of the lightbox using 10 cm spacings. At each of the marked positions the intensity of the tubes were noted using a silicon photodiode and linear amplifier..

Results

Position	Error	Reading	Reading	Reading	Mean	SE
-30.00	0.20	1.28	1.24	1.21	1.24	0.02
-22.50	0.20	1.40	1.44	1.39	1.41	0.01
-15.00	0.20	1.56	1.61	1.52	1.56	0.02
-7.50	0.20	1.62	1.69	1.60	1.64	0.02
0.00	0.20	1.70	1.70	1.62	1.67	0.02
7.50	0.20	1.70	1.68	1.61	1.66	0.02
15.00	0.20	1.63	1.62	1.51	1.59	0.03
22.50	0.20	1.50	1.53	1.42	1.48	0.03
30.00	0.20	1.38	1.37	1.30	1.35	0.02
			30 cm LAMP SPACING			

Position	Reading	Reading	Reading	Mean	SE	Error
-30.00	1.29	1.33	1.33	1.32	0.01	0.20
-22.50	1.55	1.46	1.53	1.51	0.02	0.20
-15.00	1.70	1.55	1.62	1.62	0.04	0.20
-7.50	1.74	1.64	1.63	1.67	0.03	0.20
0.00	1.74	1.74	1.60	1.69	0.04	0.20
7.50	1.65	1.68	1.51	1.61	0.04	0.20
15.00	1.45	1.54	1.39	1.46	0.04	0.20
22.50	1.21	1.40	1.19	1.27	0.06	0.20
30.00	1.01	1.33	1.05	1.13	0.08	0.20
			20cm LAMP SPACING			

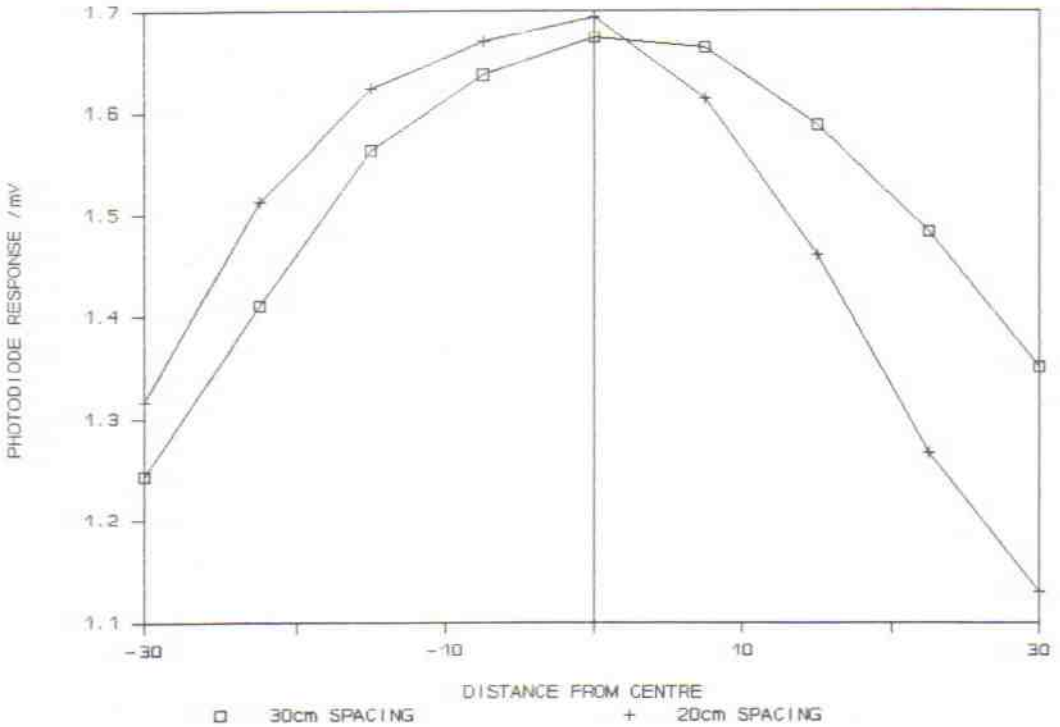

Figure 4.2.1 Initial Spectrum obtained from the lightboxes

Experiment 2: From these results a further experiment was carried out using the same method as above, but with the tubes re- positioned to try and give a more evenly spread spectrum. The spread of light intensity was more even, but we still needed to optimise the parameters further.

Results

Position	Error	Reading	Reading	Reading	Mean	SE
-30.00	0.20	1.28	1.24	1.21	1.24	0.02
-22.50	0.20	1.40	1.44	1.39	1.41	0.01
-15.00	0.20	1.56	1.61	1.52	1.56	0.02
-7.50	0.20	1.62	1.69	1.60	1.64	0.02
0.00	0.20	1.70	1.70	1.62	1.67	0.02
7.50	0.20	1.70	1.68	1.61	1.66	0.02
15.00	0.20	1.63	1.62	1.51	1.59	0.03
22.50	0.20	1.50	1.53	1.42	1.48	0.03
30.00	0.20	1.38	1.37	1.30	1.35	0.02
			30 cm LAMP SPACING			

Position	Reading	Reading	Reading	Mean	SE
-30.00	1.29	1.33	1.33	1.32	0.01
-22.50	1.55	1.46	1.53	1.51	0.02
-15.00	1.70	1.55	1.62	1.62	0.04
-7.50	1.74	1.64	1.63	1.67	0.03
0.00	1.74	1.74	1.60	1.69	0.04
7.50	1.65	1.68	1.51	1.61	0.04
15.00	1.45	1.54	1.39	1.46	0.04
22.50	1.21	1.40	1.19	1.27	0.06
30.00	1.01	1.33	1.05	1.13	0.08
			20cm LAMP SPACING		

Position	Error	Reading	Reading	Reading	Mean	SE
-20.00	0.20	2.33	2.29	2.26	2.29	0.02
-15.00	0.20	2.26	2.38	2.31	2.32	0.03
-10.00	0.20	2.41	2.42	2.41	2.41	0.00
-5.00	0.20	2.50	2.51	2.47	2.49	0.01
0.00	0.20	2.55	2.55	2.53	2.54	0.01
5.00	0.20	2.52	2.56	2.48	2.52	0.02
10.00	0.20	2.44	2.47	2.45	2.45	0.01
15.00	0.20	2.45	2.29	2.30	2.35	0.04
20.00	0.20	2.39	2.28	2.30	2.32	0.03
		X=0				

Position	Error	Reading	Reading	Reading	Mean	SE
-20.00	0.20	1.99	1.96	1.98	1.98	0.01
-15.00	0.20	2.02	2.03	2.01	2.02	0.00
-10.00	0.20	2.08	2.09	2.09	2.09	0.00
-5.00	0.20	2.11	2.12	2.10	2.11	0.00
0.00	0.20	2.12	2.10	2.09	2.10	0.01
5.00	0.20	2.07	2.06	2.05	2.06	0.00
10.00	0.20	1.99	1.97	1.99	1.98	0.01
15.00	0.20	1.90	1.86	1.89	1.88	0.01
20.00	0.20	1.81	1.79	1.79	1.80	0.01
			X=30			

Position	Error	Reading	Reading	Reading	Mean	SE
-20.00	0.20	1.99	1.96	1.98	1.98	0.01
-15.00	0.20	2.02	2.03	2.01	2.02	0.00
-10.00	0.20	2.08	2.09	2.09	2.09	0.00
-5.00	0.20	2.11	2.12	2.10	2.11	0.00
0.00	0.20	2.12	2.10	2.09	2.10	0.01
5.00	0.20	2.07	2.06	2.05	2.06	0.00
10.00	0.20	1.99	1.97	1.99	1.98	0.01
15.00	0.20	1.90	1.86	1.89	1.88	0.01
20.00	0.20	1.81	1.79	1.79	1.80	0.01
			X=30			

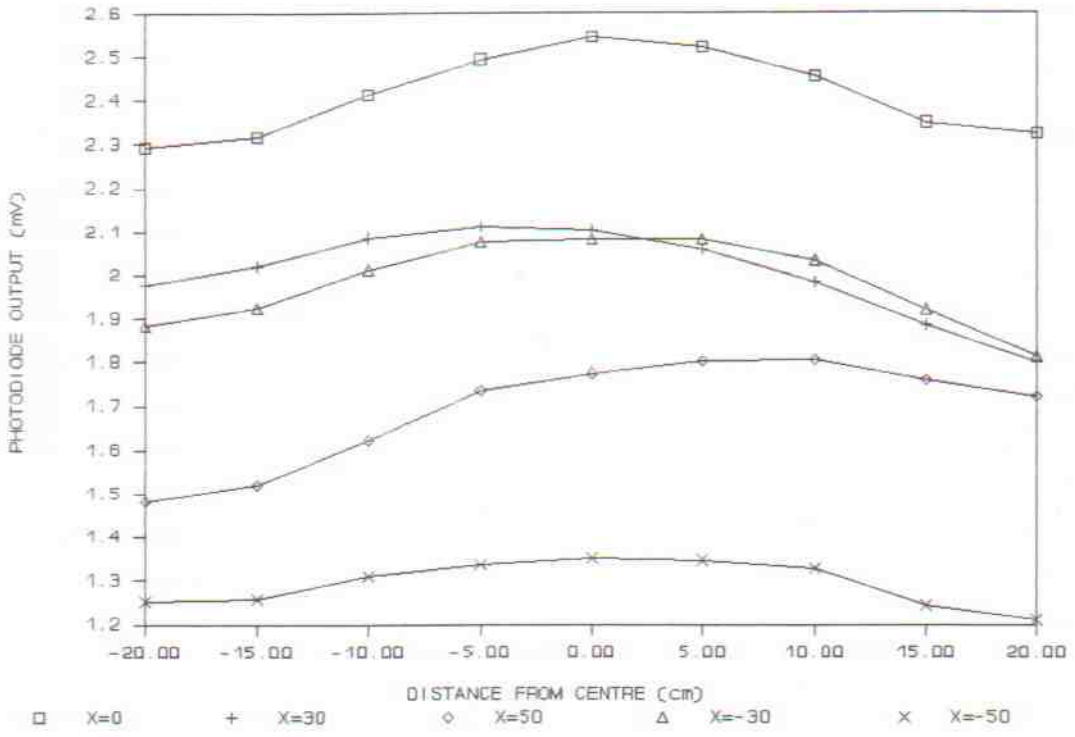

Figure 4.2.2 Light Spectrum obtained from re- positioning the tube configurations

Experiment 3: The same method as above was applied, but this time all the sides of the lightbox covered with reflectors.

Results

Position	Error	Reading	Reading	Reading	Mean	SE
-30.00	0.20	1.28	1.24	1.21	1.24	0.02
-22.50	0.20	1.40	1.44	1.39	1.41	0.01
-15.00	0.20	1.56	1.61	1.52	1.56	0.02
-7.50	0.20	1.62	1.69	1.60	1.64	0.02
0.00	0.20	1.70	1.70	1.62	1.67	0.02
7.50	0.20	1.70	1.68	1.61	1.66	0.02
15.00	0.20	1.63	1.62	1.51	1.59	0.03
22.50	0.20	1.50	1.53	1.42	1.48	0.03
30.00	0.20	1.38	1.37	1.30	1.35	0.02
			30 cm LAMP SPACING			

Position	Reading	Reading	Reading	Mean	SE	Error
-30.00	1.29	1.33	1.33	1.32	0.01	0.20
-22.50	1.55	1.46	1.53	1.51	0.02	0.20
-15.00	1.70	1.55	1.62	1.62	0.04	0.20
-7.50	1.74	1.64	1.63	1.67	0.03	0.20
0.00	1.74	1.74	1.60	1.69	0.04	0.20
7.50	1.65	1.68	1.51	1.61	0.04	0.20
15.00	1.45	1.54	1.39	1.46	0.04	0.20
22.50	1.21	1.40	1.19	1.27	0.06	0.20
30.00	1.01	1.33	1.05	1.13	0.08	0.20
			20cm LAMP SPACING			

Position	Error	Reading	Reading	Reading	Mean	SE
-20.00	0.20	2.33	2.29	2.26	2.29	0.02
-15.00	0.20	2.26	2.38	2.31	2.32	0.03
-10.00	0.20	2.41	2.42	2.41	2.41	0.00
-5.00	0.20	2.50	2.51	2.47	2.49	0.01
0.00	0.20	2.55	2.55	2.53	2.54	0.01
5.00	0.20	2.52	2.56	2.48	2.52	0.02
10.00	0.20	2.44	2.47	2.45	2.45	0.01
15.00	0.20	2.45	2.29	2.30	2.35	0.04
20.00	0.20	2.39	2.28	2.30	2.32	0.03
		X=0				

Position	Error	Reading	Reading	Reading	Mean	SE
-20.00	0.20	1.99	1.96	1.98	1.98	0.01
-15.00	0.20	2.02	2.03	2.01	2.02	0.00
-10.00	0.20	2.08	2.09	2.09	2.09	0.00
-5.00	0.20	2.11	2.12	2.10	2.11	0.00
0.00	0.20	2.12	2.10	2.09	2.10	0.01
5.00	0.20	2.07	2.06	2.05	2.06	0.00
10.00	0.20	1.99	1.97	1.99	1.98	0.01
15.00	0.20	1.90	1.86	1.89	1.88	0.01
20.00	0.20	1.81	1.79	1.79	1.80	0.01
			X=30			

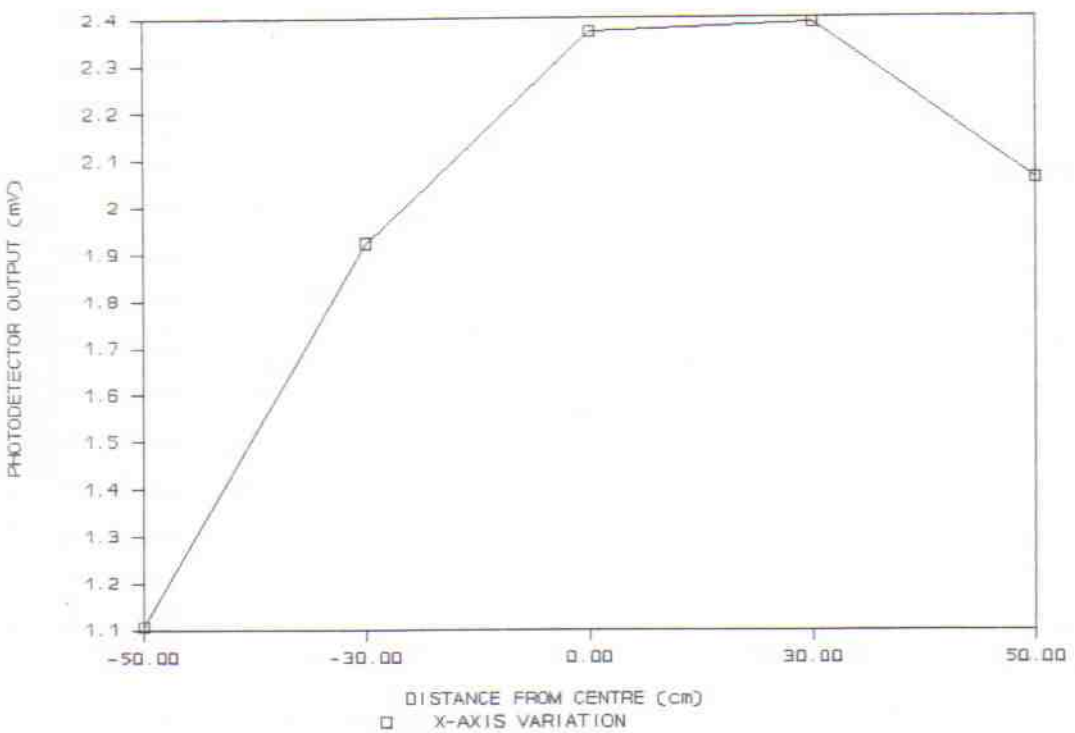

Figure 4.2.3 Light Spectrum obtained from reflectors placed on the inside walls of the lightboxes

Experiment 4: Again the same method was applied with the latest tube configuration, but this time with the addition of a white paper base reflector, with the intensities taken from the marked positions using a photodetector.

From the use of a reflector we were able to see a large improvement in the spread of the spectrum.

Results

Position	Error	Reading	Reading	Reading	Mean	SE
-30.00	0.20	1.28	1.24	1.21	1.24	0.02
-22.50	0.20	1.40	1.44	1.39	1.41	0.01
-15.00	0.20	1.56	1.61	1.52	1.56	0.02
-7.50	0.20	1.62	1.69	1.60	1.64	0.02
0.00	0.20	1.70	1.70	1.62	1.67	0.02
7.50	0.20	1.70	1.68	1.61	1.66	0.02
15.00	0.20	1.63	1.62	1.51	1.59	0.03
22.50	0.20	1.50	1.53	1.42	1.48	0.03
30.00	0.20	1.38	1.37	1.30	1.35	0.02
			30 cm LAMP SPACING			

Reading	Reading	Reading	Mean	SE	Error	Position
1.29	1.33	1.33	1.32	0.01	0.20	-30.00
1.55	1.46	1.53	1.51	0.02	0.20	-22.50
1.70	1.55	1.62	1.62	0.04	0.20	-15.00
1.74	1.64	1.63	1.67	0.03	0.20	-7.50
1.74	1.74	1.60	1.69	0.04	0.20	0.00
1.65	1.68	1.51	1.61	0.04	0.20	7.50
1.45	1.54	1.39	1.46	0.04	0.20	15.00
1.21	1.40	1.19	1.27	0.06	0.20	22.50
1.01	1.33	1.05	1.13	0.08	0.20	30.00
		20cm LAMP SPACING				

Position	Error	Reading	Reading	Reading	Mean	SE
-20.00	0.20	2.33	2.29	2.26	2.29	0.02
-15.00	0.20	2.26	2.38	2.31	2.32	0.03
-10.00	0.20	2.41	2.42	2.41	2.41	0.00
-5.00	0.20	2.50	2.51	2.47	2.49	0.01
0.00	0.20	2.55	2.55	2.53	2.54	0.01
5.00	0.20	2.52	2.56	2.48	2.52	0.02
10.00	0.20	2.44	2.47	2.45	2.45	0.01
15.00	0.20	2.45	2.29	2.30	2.35	0.04
20.00	0.20	2.39	2.28	2.30	2.32	0.03
		X=0				

Position	Error	Reading	Reading	Reading	Mean	SE
-20.00	0.20	1.99	1.96	1.98	1.98	0.01
-15.00	0.20	2.02	2.03	2.01	2.02	0.00
-10.00	0.20	2.08	2.09	2.09	2.09	0.00
-5.00	0.20	2.11	2.12	2.10	2.11	0.00
0.00	0.20	2.12	2.10	2.09	2.10	0.01
5.00	0.20	2.07	2.06	2.05	2.06	0.00
10.00	0.20	1.99	1.97	1.99	1.98	0.01
15.00	0.20	1.90	1.86	1.89	1.88	0.01
20.00	0.20	1.81	1.79	1.79	1.80	0.01
			X=30			

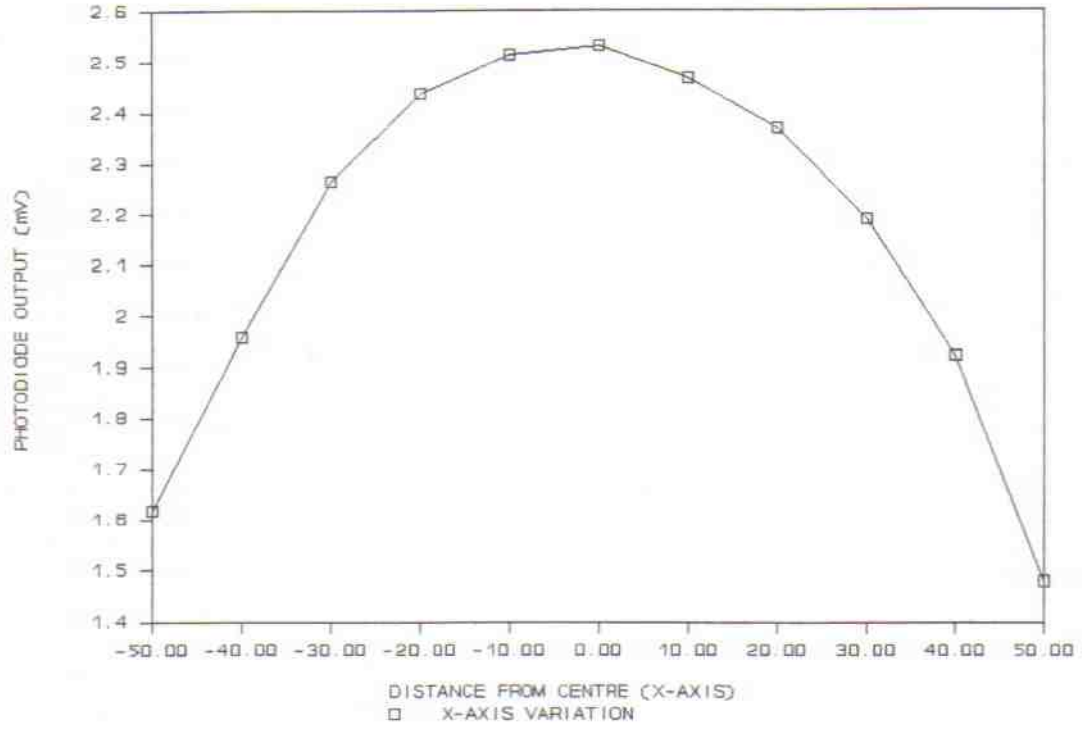

Figure 4.2.4 Light Spectrum obtained from lightboxes with reflectors placed on every wall

Conclusion: The final experiment gave the best intensity results and most evenly spread light spectrum. The next progression is to obtain a more permanent arrangement with respect to the reflectors. A high reflectance paint - TiO2 paint was obtained and each interior of the lightboxes were painted with two coats. This gave a safer and more permanent effect than the use of paper reflectors.

Experiment 5 **Light Box Absolute Power Density Measurements**

The Pyroelectric radiometer was switched on and allowed to warm up for at least two hours before any measurements were made. After the warm up period, the radiometer was zeroed with the front bezel rotated to the 'zero' position. The response time was set on fast and then the measurements were made.

For each light box, the power density at the centre of the box was measured first every 15° rotating vertically from the back of the box to the front and then every 30° vertically from left to right. The summation to derive the total power density as seen by an object at the centre of the box over a 2π solid angle was as follows;
The radiometer has a 0.1 Sr field of view which is equivalent to $\pm\ 10^{\circ}$ in the vertical plane (according to manufacturers data). Measurements were made every 15° hence there is a 5° overlap between each measurement and the preceding one, consequently to correct these measurements for n overlap, each power density measurement was multiplied by a factor of 0.75. The summation used was as follows;

$$P_{Total} = \sum_{i=1}^{n} \frac{P(\theta)_i}{P_{centre}} \sum_{i=1}^{m} \frac{3}{4} P(\phi)_i$$

$$= \frac{3}{4} \sum_{i=1}^{n} \frac{p(\theta)_i}{P_{centre}} \sum_{i=1}^{m} P(\phi)_i$$

where:

P_{centre} refers to the central vertical power density measurement.

$P(\theta)$ = power density measurements from left to right

$P(\phi)$ = power density measurements from front to back

Properly the P(θ) measurements should also be corrected to provide a continuous bandwidth across the box, however this was not done in order to allow for some of the loss that will occur in directions towards the corners of the box. The total power calculated will, of course, be an upper limit

A) Artificial Daylight.

Angle / degrees	Power Density / μWcm^{-2}	
	Front to Back	Left to Right
0	74	75
15	75	-----
30	82	101
45	101	-----
60	189	117
75	188	-----
90	112	108
105	184	-----
120	185	113
135	100	-----
150	90	120
165	80	-----
180	76	74

Total Power Density = 7.292 $mWcm^{-2}$

hence 1 Jcm^{-2} will be delivered in 137 seconds or 2 minutes 17 seconds.

B) Natural Deluxe.

Angle / degrees	Power Density / μWcm^{-2}	
	Front to Back	Left to Right
0	57	78
15	82	-----
30	92	114
45	113	-----
60	202	114
75	166	-----
90	112	109
105	157	-----
120	212	119
135	118	-----
150	115	102
165	84	-----
180	86	80

Total Power Density = 7.704 $mWcm^{-2}$

hence 1 Jcm^{-2} will be delivered in 130 seconds or 2 minutes 10 seconds.

4.3 Bleaching of TL From Mangos -Comparison of Light Sources

Having optimised and calibrated the uniformity and total power delivered to a sample in a preset time for experimental purposes, a series of experiments was undertaken to evaluate the effect of bleaching on samples. The first experiment was designed to establish the differences between the two light boxes when a set of samples was exposed to the same energy level. It was recognised from previous experience with fruits and vegetables that extensive replication would be needed to overcome intrinsic variability, therefore a decision was taken to limit the investigation to one food type in the first instance. After consulation with MAFF mangos were selected, since they are a fruit class which benefits from irradiation, and which is known to be irradiated in some overseas plants.

Tenfold replications was selected for these experiments, and a decsion to examine the comparative effects of bleaching to 1 J cm^{-2} was taken. Two boxes of South African mangos were purchased from a local wholesaler and importer of tropical foods, and the following experiment conducted with a subset of 40 mangos.

To ensure all relevant variables were controlled the 40 mango's (SP441) were used and split in the following manner;

10 Unirradiated Controls, stored in the dark
10 Irradiated Controls (1 kGy), stored in the dark
10 Irradiated to 1 kGy and bleached in the Natural Deluxe light box
10 Irradiated to 1 kGy and bleached in the Artificial Daylight light box.

Hence a total of 30 mangos was irradiated to 1 kGy in six batches of 5 and then stored in a fridge with the unirradiated controls until ready for separation. The sets of ten that were to be bleached were exposed to the lightboxes just prior to separation in the following manner;

Batch 1 and Batch 2 were exposed for 2' 10'' in the natural deluxe light box (= 1 Jcm^{-2})

Batch 5 and Batch 6 were exposed for 2' 17'' in the artificial daylight light box (= 1 Jcm^{-2})

The light boxes were monitored before and during the bleaching experiment to ensure that they were operating correctly, and that the illumination levels were the same as had applied during the absolute calibration experiments. The photodiode responses were as follows.

Light Box	Photo Diode Voltage / V	
	11/12/91	18/12/91
Natural Deluxe	6.60 $\pm$ 0.2	6.53
Artificial Daylight	6.45 $\pm$ 0.2	6.66

It can be seen that the voltages are of a similar order of magnitude to the original readings and within the error limit of 0.2 Volts, indicating that the response of the light boxes was unchanged and the calibrated the power densities were applicable.

Light Box Bleaching Tests - Mangos

The minerals from the mangos were separated using the method developed for fruits. Each mango was immersed in water and agitated in the ultrasonic bath for approximately 30 minutes. The mangos were then removed from the water and the residue left to stand for about 1 hour, the surplus water was then decanted off, leaving behind enough to ensure that no mineral grains were lost. This was then transferred to a centrifuge tube and spun at 3000 rpm for a few minutes to force the mineral grains to the bottom to allow the rest of the water to be decanted off. Organics were removed using the density separation method with tungstate. The mineral grains were then washed well with de-ionised water and then etched in 1M HCl for about 15 minutes. After this acid etch, the solution was neutralised in ammonia, washed in de-ionised water, rinsed in acetone and then suspended in acetone over blanked disks and dried down overnight at 55°C. The discs were then subject to standard TL measurements with a normalising second dose of 1 kGy.

The results from the control set are shown in figures 4.3.1 - 4.3.8, as a sequence of glow ratio histograms and first glow vs second glow plots at different temperature bands through the glow curve. There is clear evidence that the irradiated unbleached controls are well

resolved at all temperatures, although the discrimination is poorer at high temperatures due the presence of a greater residual geological signal in unirradiated samples.

Similar diagrams are presented for both bleached sets in figures 4.3.9 - 4.3.24. It is evident that in both sets, the discrimination between irradiated and unirradiated samples has been reduced slightly. This reduction in the discriminating gap can be observed in the glow ratio histogram, figures 4.3.9 - 4.3.16, of mangos bleached with the Artificial Daylight tubes. Also in the plot of 250 - 300 °C ratio histogram, figure 4.3.15 shows a severe narrowing of the discriminating gap probably due to the increase in the geological signal.

It is notable that the artificial daylight source appears to be somewhat more effective in reducing signal levels, but that even in the worst case the mean signal after bleaching is still able to discriminate between irradiated and unirradiated samples. It also appears that bleached samples show a greater heterogeneity of TL response, perhaps indicating that partial self shielding of samples illuminated from one side, and the different photosensitivity of the minerals contained on each surface.

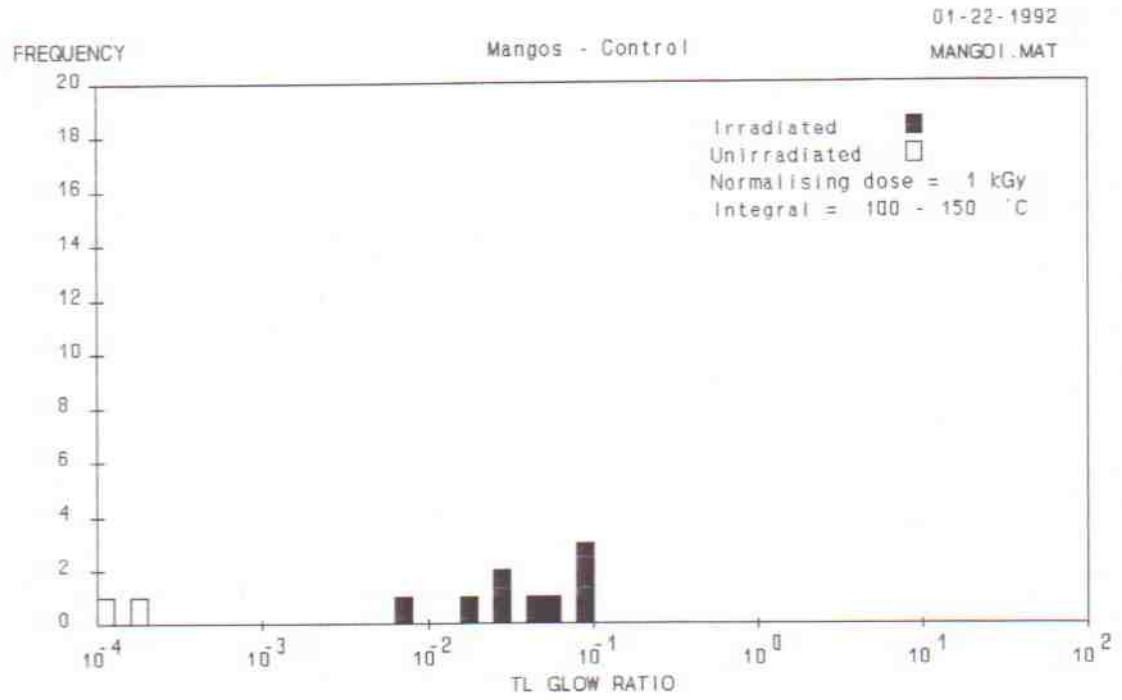

Figure 4.3.1 Glow Ratio Histogram for the 100-150 °C Integral for Control Set of Mangos

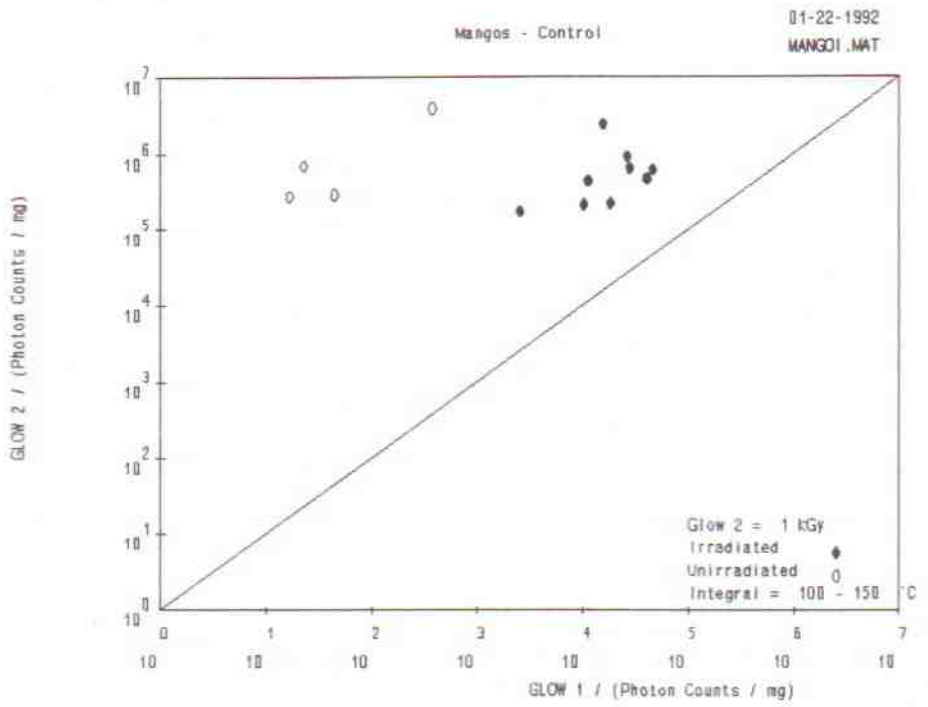

Figure 4.3.2 First glow vs second glow plot fot the 100-150 °C Integral for the Control Set of Mangos

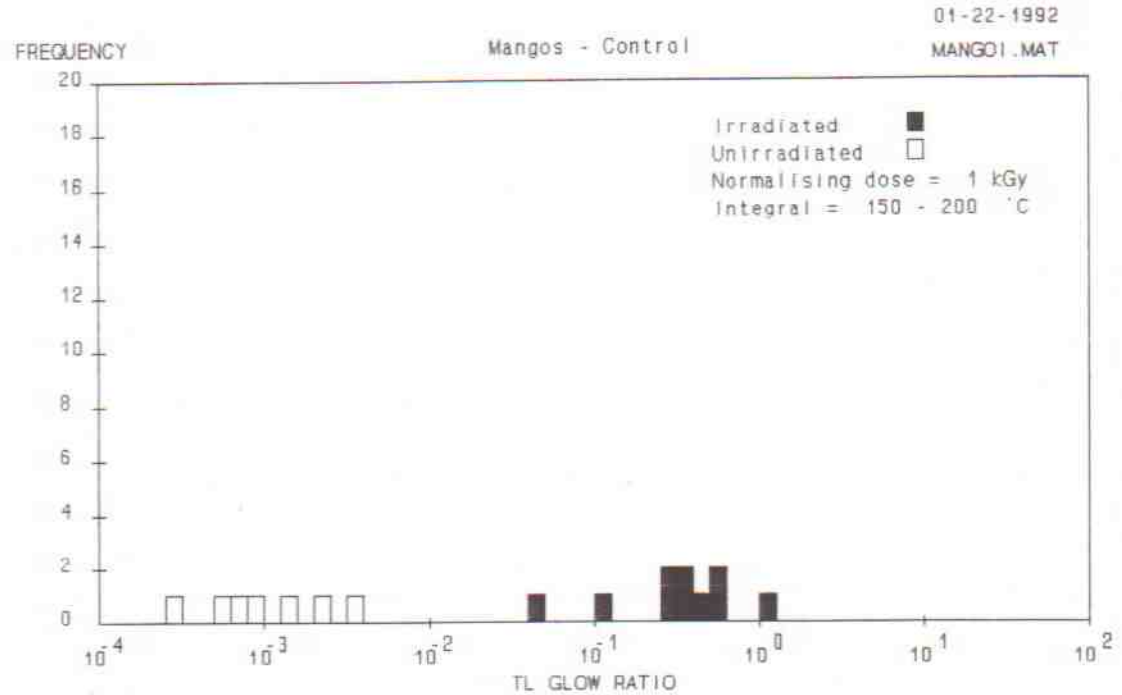

Figure 4.3.3 Glow Ratio Histogram for the 150-200 °C Integral for the Control Set of Mangos

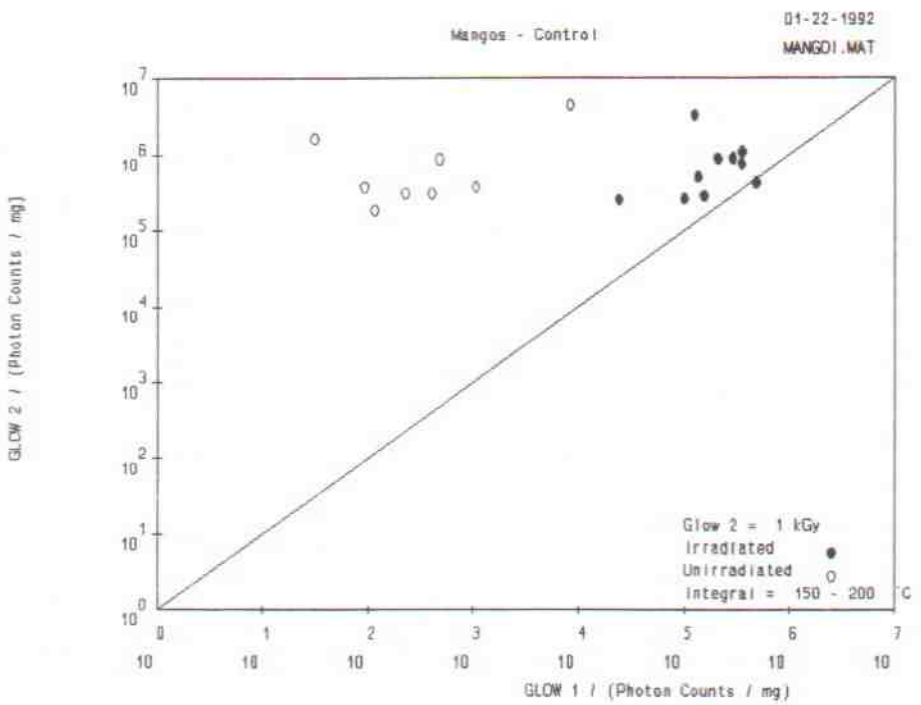

Figure 4.3.4 First glow vs second glow plot for the 150-200 °C Integral for the Control Set of Mangos

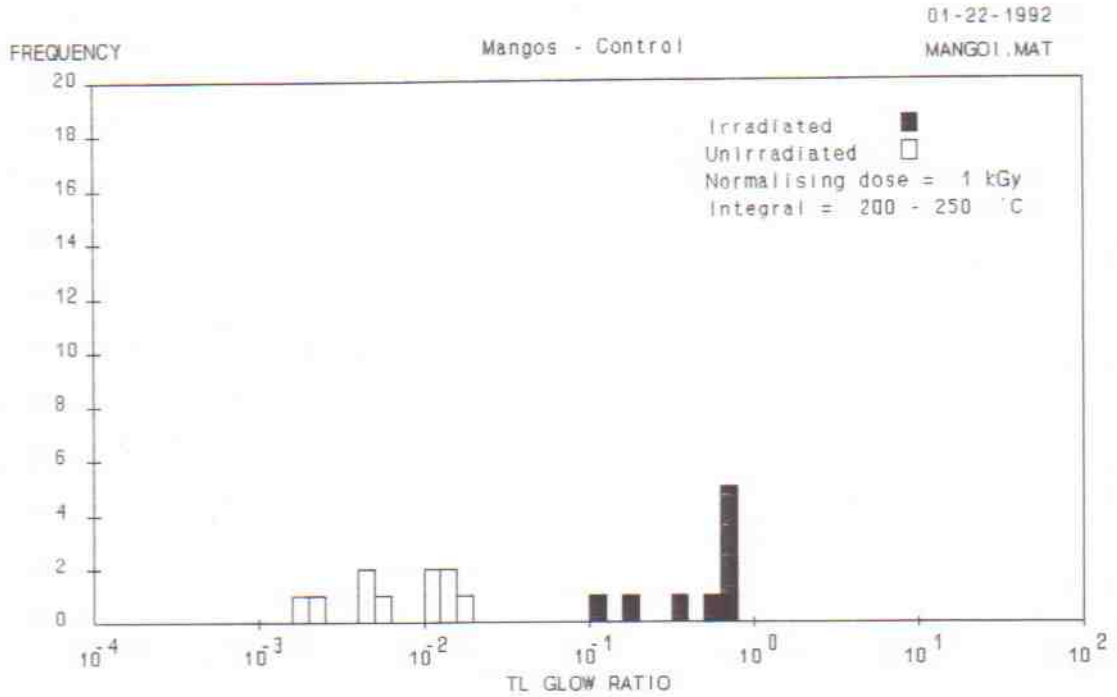

Figure 4.3.5 Glow Ratio Histogram for the 200-250 °C Integral for the Control Set of Mangos

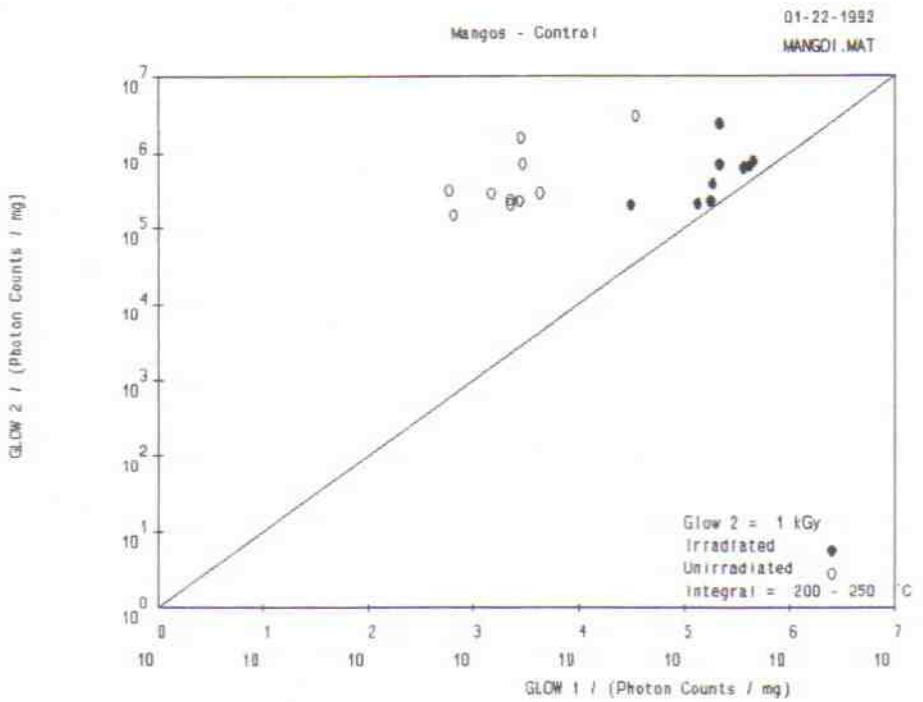

Figure 4.3.6 First glow vs second glow plot for the 200-250 °C Integralfor the Control Set of Mangos

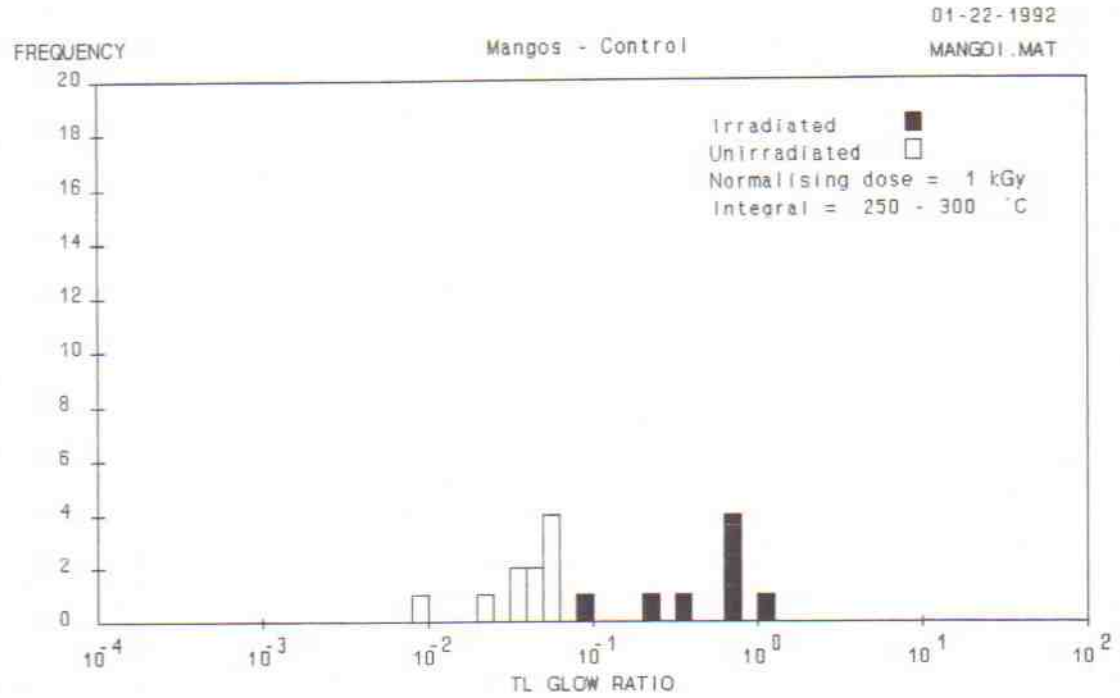

Figure 4.3.7 Glow Ratio Histogram for the 250-300°C Integral for the Control Set of Mangos

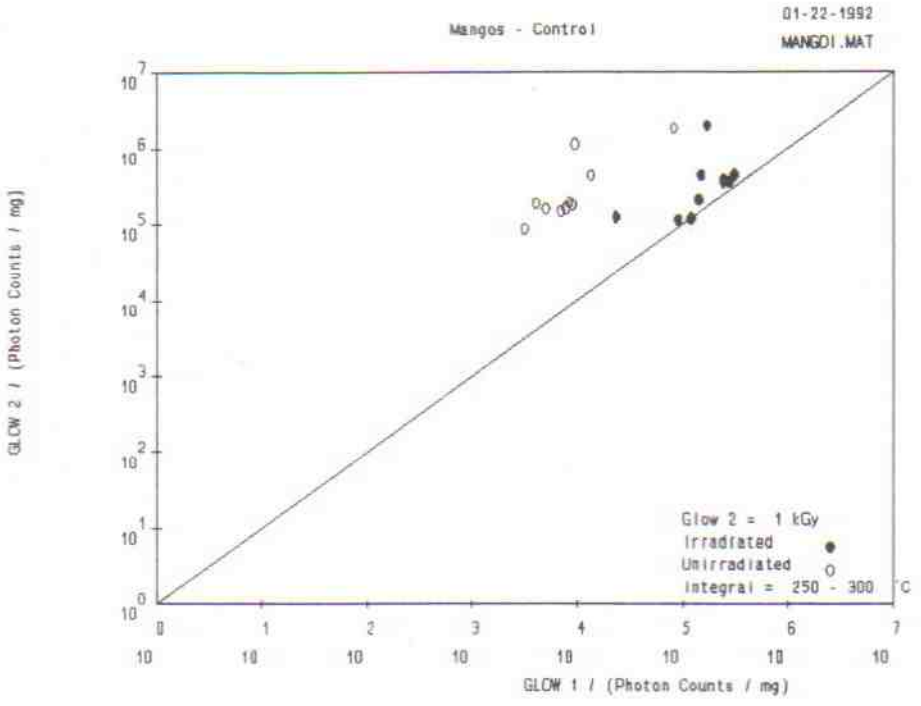

Figure 4.3.8 First glow vs second glow for the 250-300°C Integral for the Control Set of Mangos

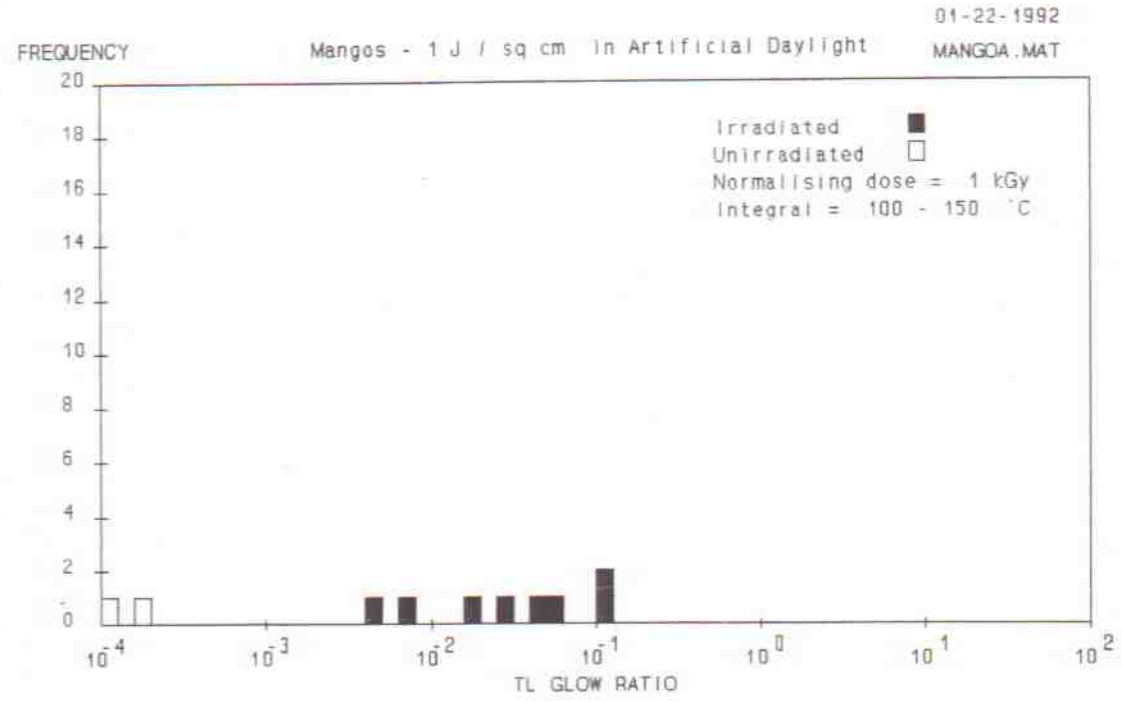

Figure 4.3.9 Glow Ratio Histogram for the 100-150 °C Integral for Mangos in Artificial Daylight

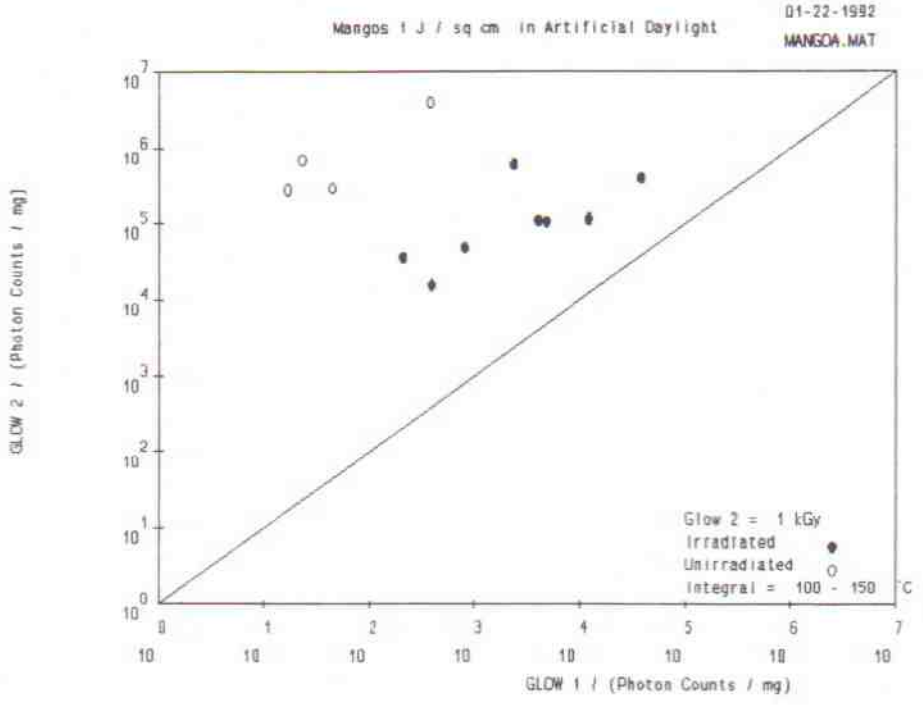

Figure 4.3.10 First glow vs second glow plot for the 100-150 °C Integral for Mangos in Artificial Daylight

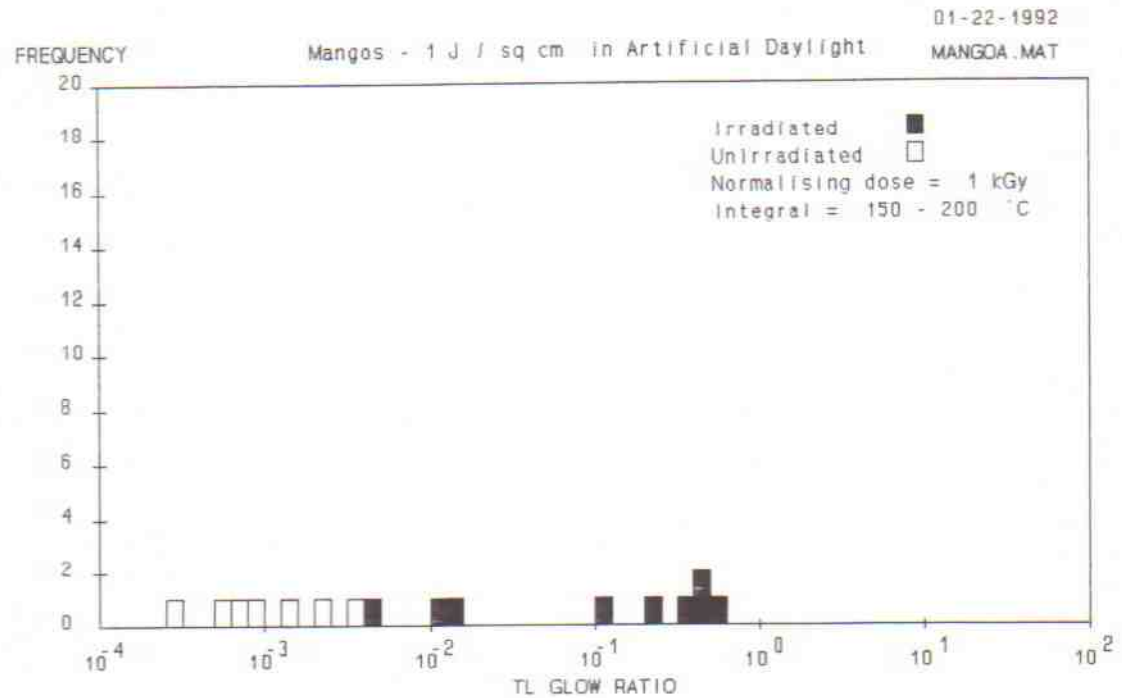

Figure 4.3.11 Glow Ratio Histogram for the 150-200 °C Integral for Mangos in Artificial Daylight

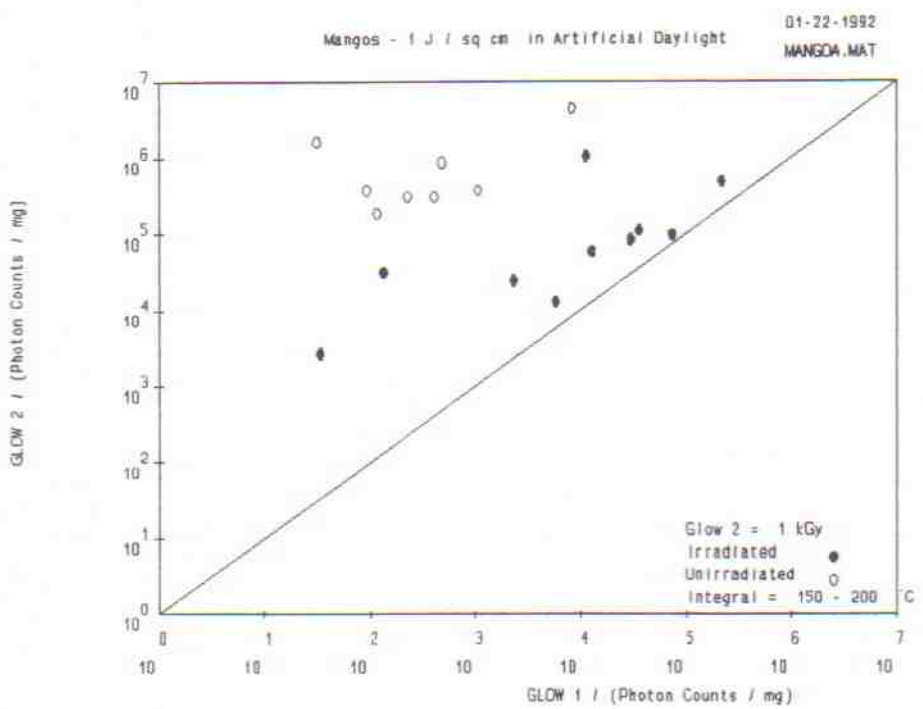

Figure 4.3.12 First glow vs second glow plot for the 150-200 °C Integral for Mangos in Artificial Daylight

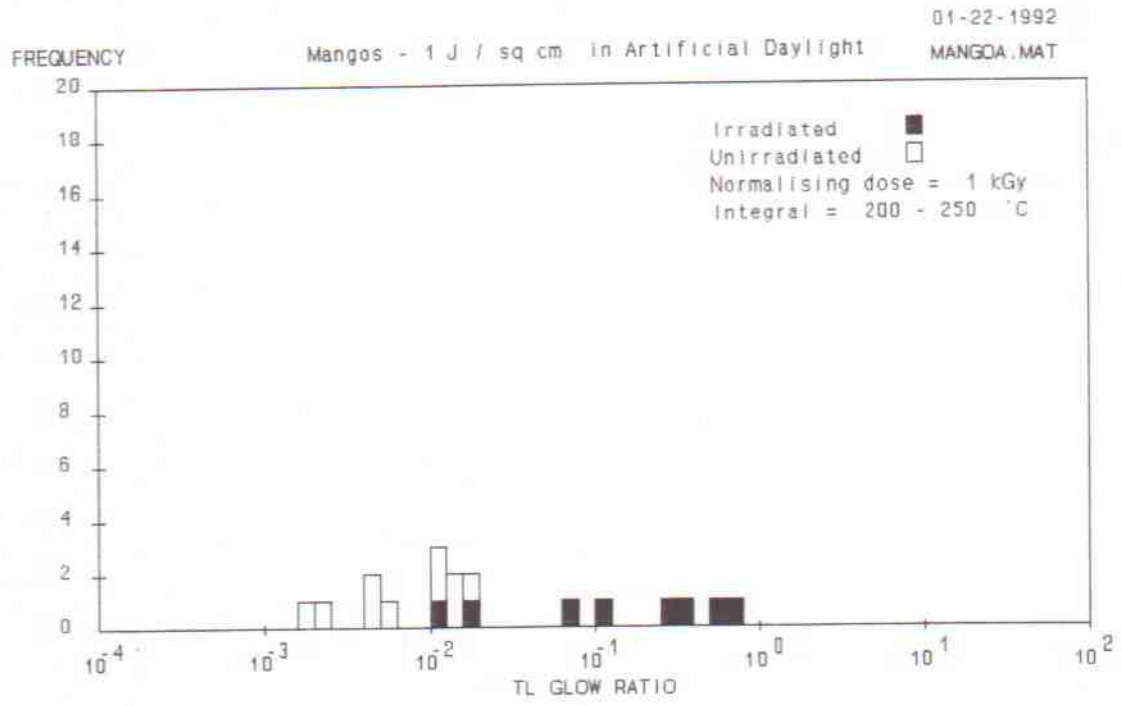

Figure 4.3.13 Glow Ratio Histogram for the 200-250 °C Integral for Mangos in Artificial Daylight

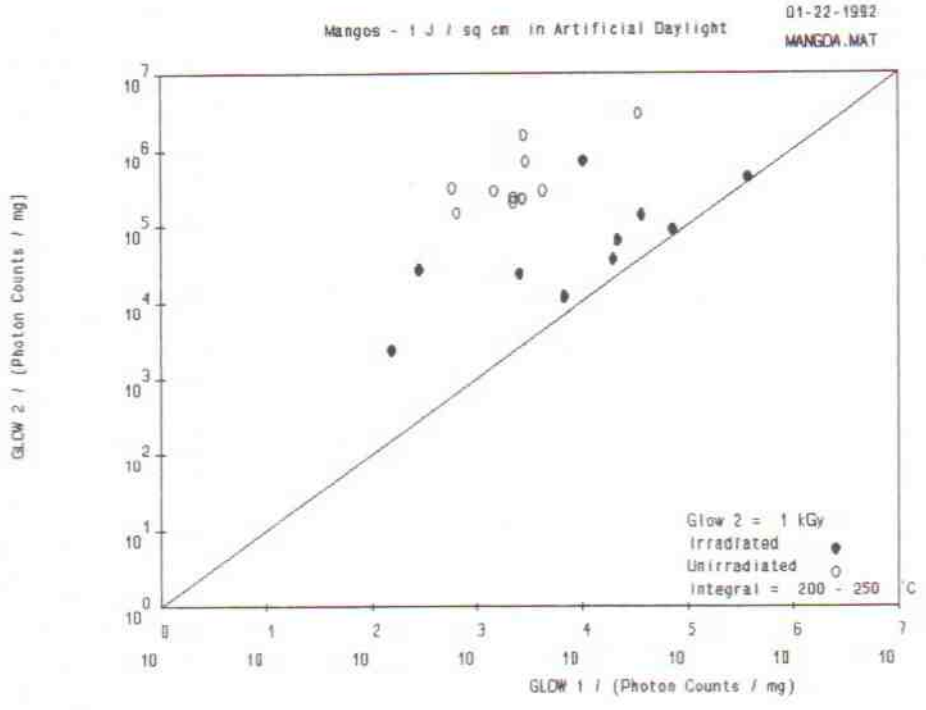

Figure 4.3.14 First glow vs second glow plot for the 200-250 °C Integral for Mangos in Artificial Daylight

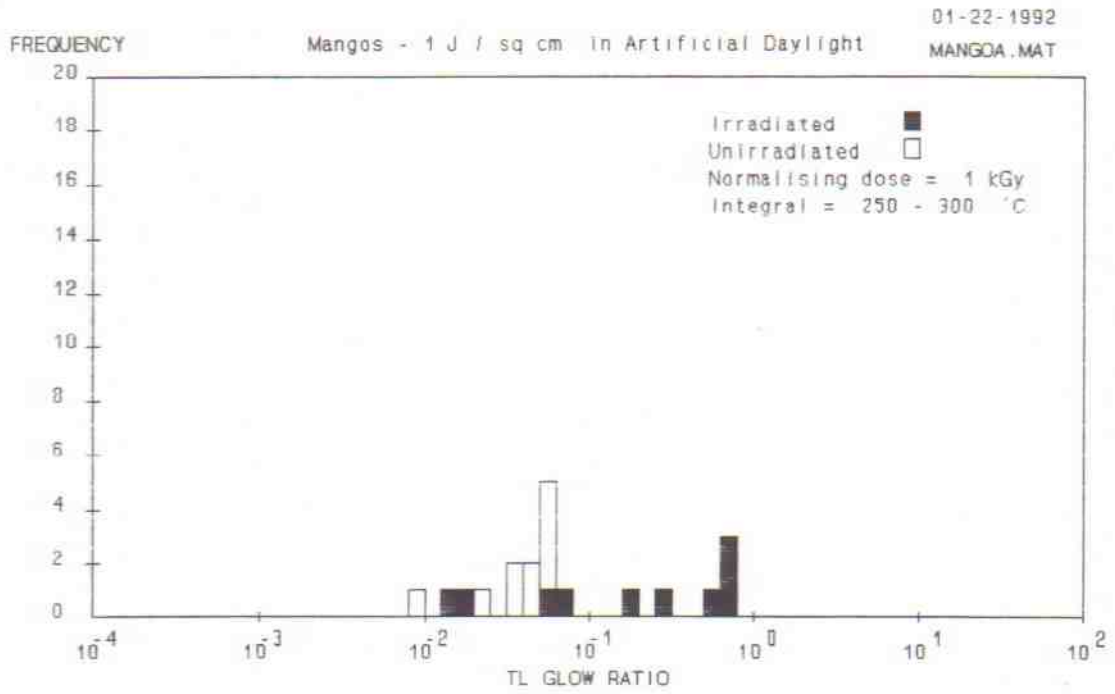

Figure 4.3.15 Glow Ratio Histogram for the 250-300 °C Integral for Mangos in Artificial Daylight

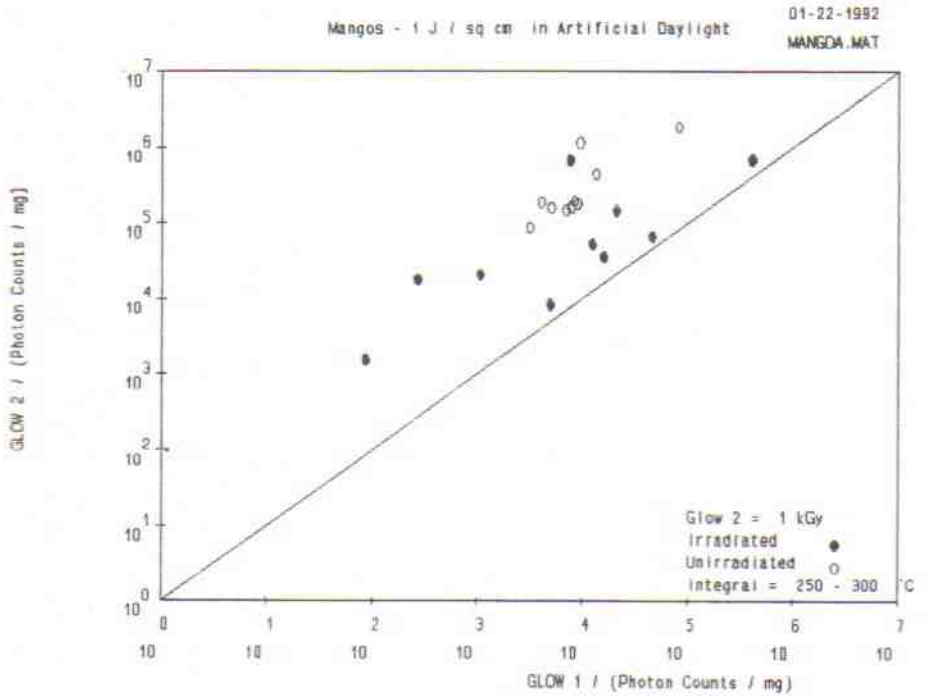

Figure 4.3.16 First glow vs second glow plot for the 250-300 °C Integral for Mangos in Artificial Daylight

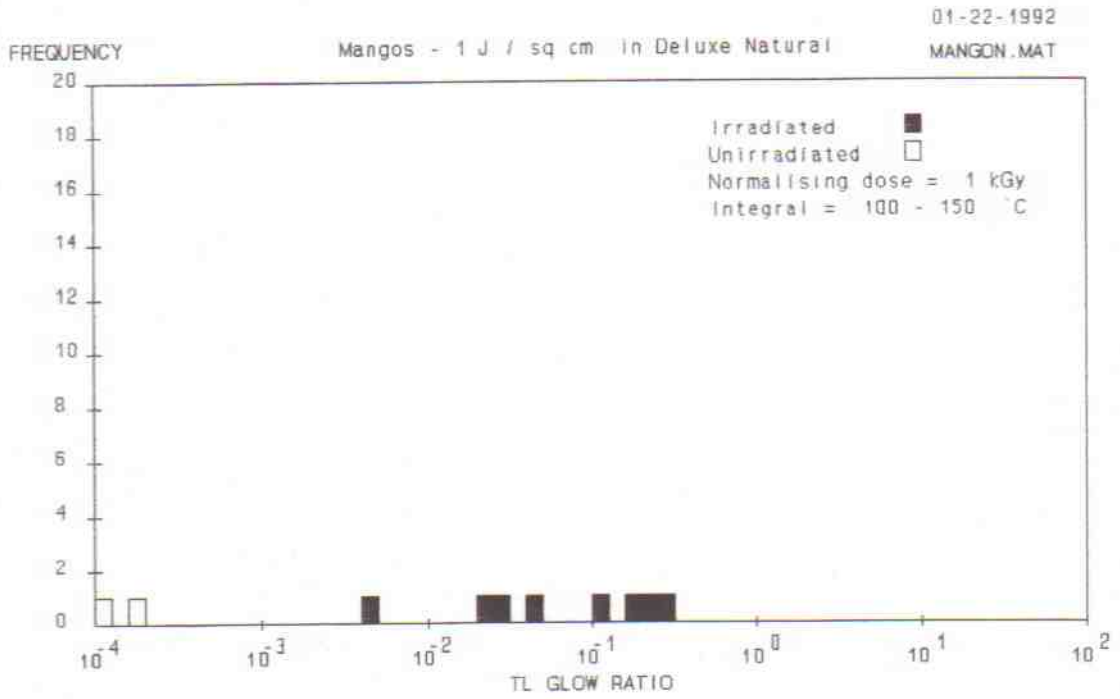

Figure 4.3.17 Glow Ratio Histogram for the 100-150 °C Integral for Mangos in Deluxe Natural

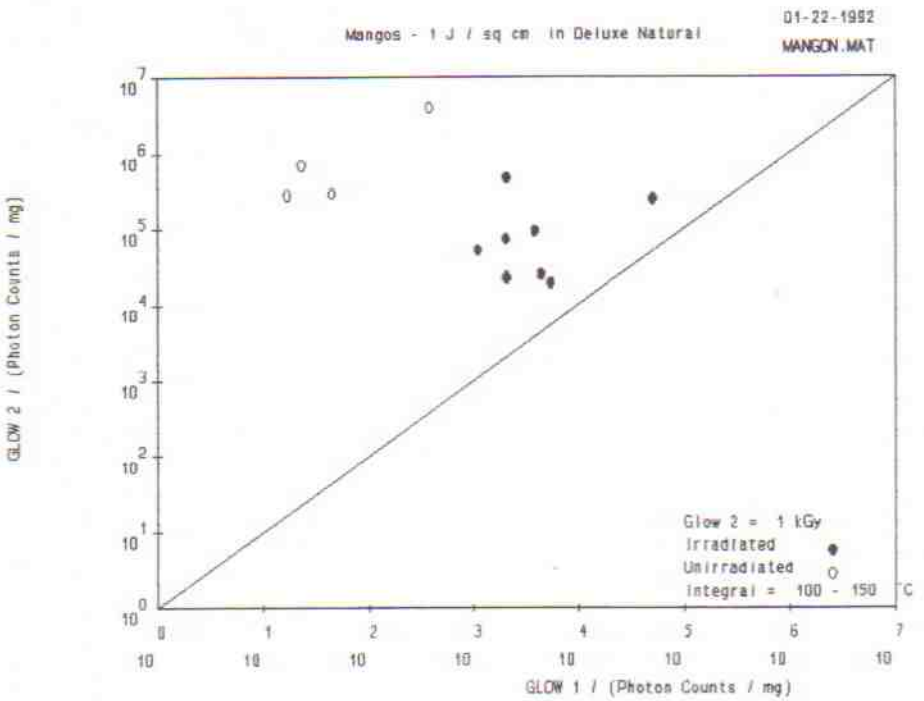

Figure 4.3.18 First glow vs second glow plot for the 100-150 °C Integral for Mangos in Deluxe Natural

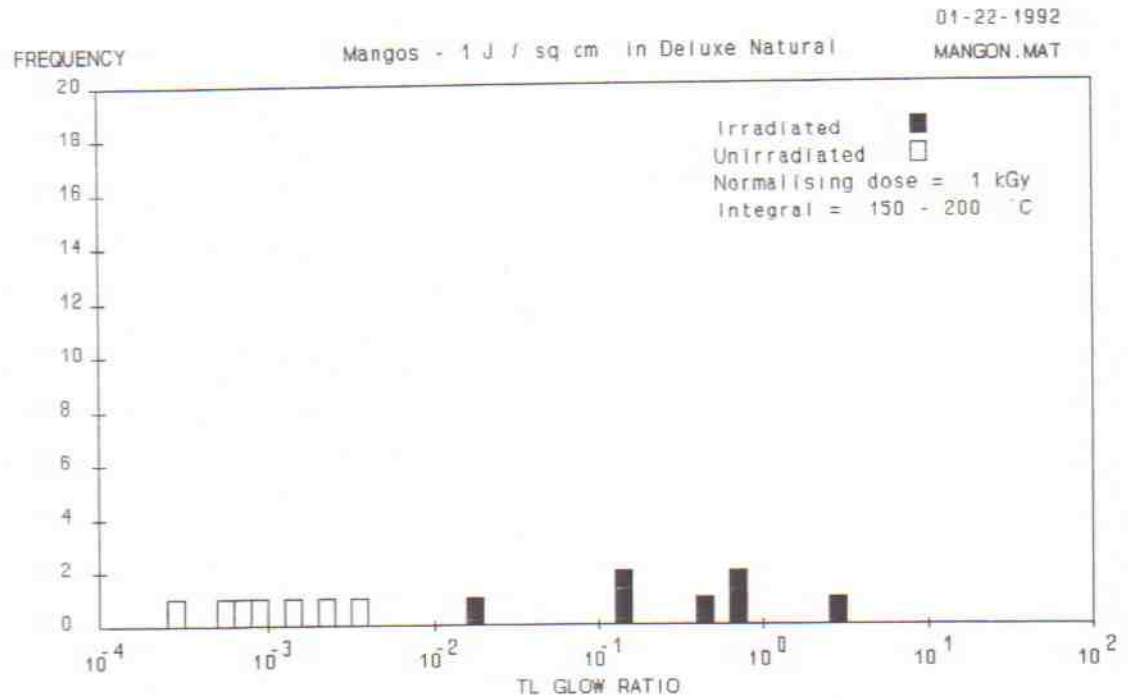

Figure 4.3.19 Glow Ratio Histogram for the 150-200°C Integral for Mangos in Deluxe Natural

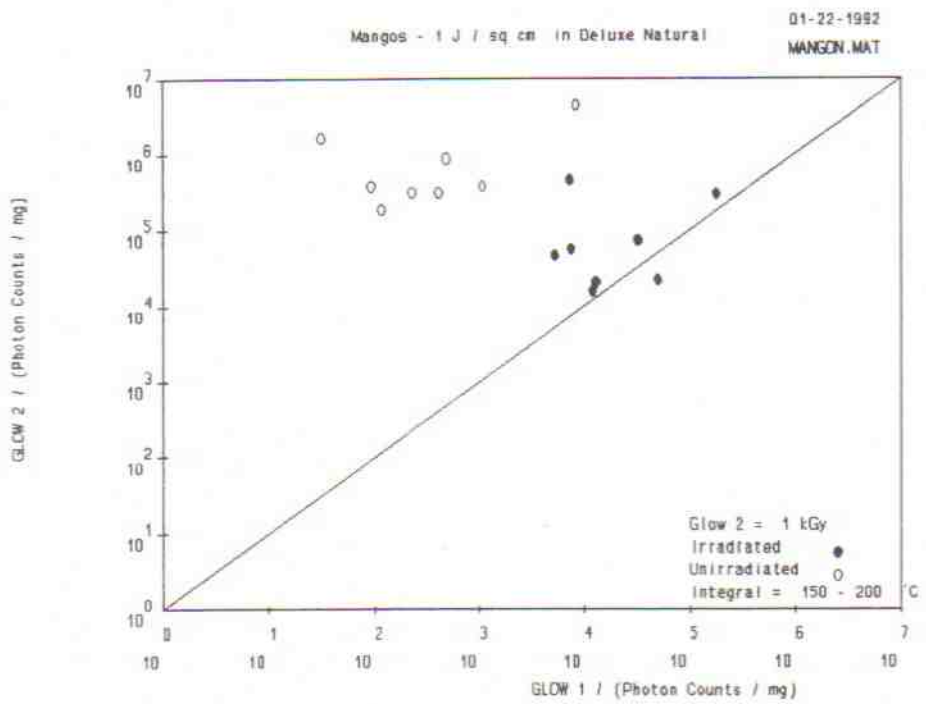

Figure 4.3.20 First glow vs second glow plot for the 150-200°C Integral for Mangos in Deluxe Natural

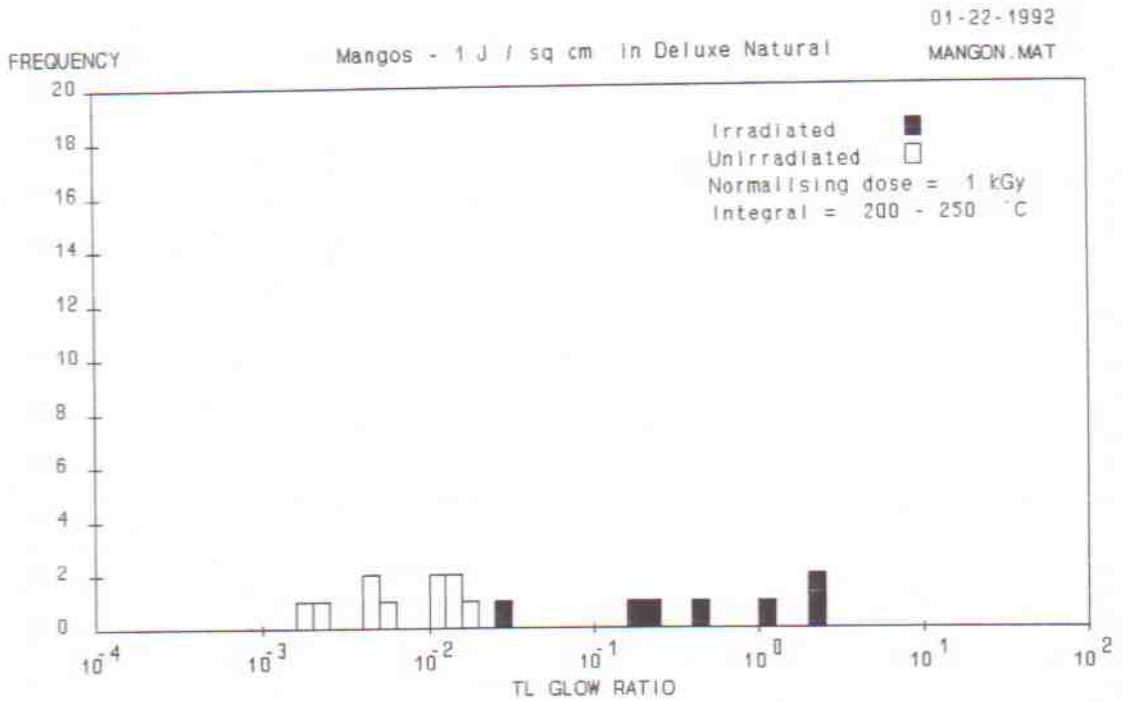

Figure 4.3.21 Glow Ratio Histogram for the 200-250 °C Integral for Mangos in Deluxe Natural

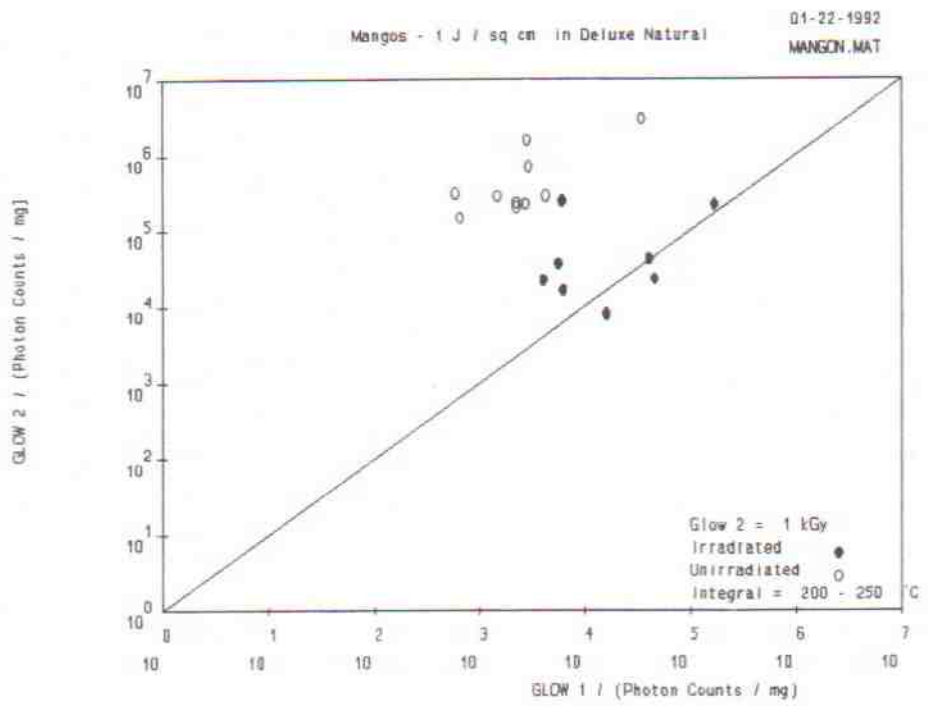

Figure 4.3.22 Concordance Plot for the 200-250 °C Integral for Mangos in Deluxe Natural

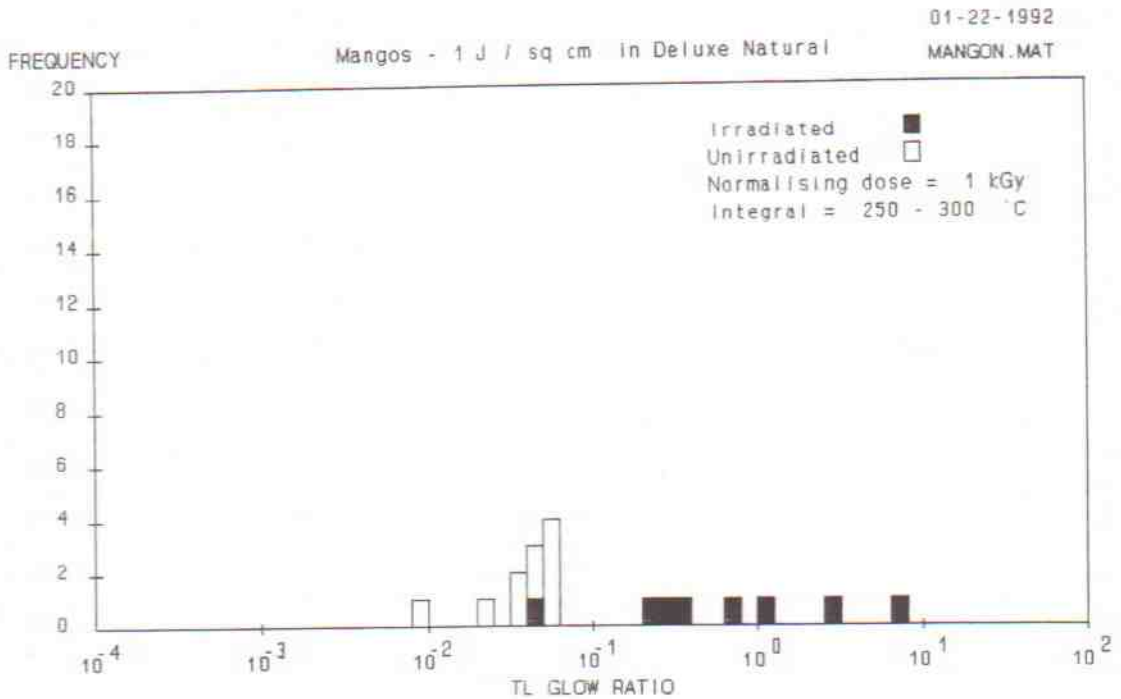

Figure 4.3.23 Glow Ratio Histogram for the 250-300°C Integral for Mangos in Deluxe Natural

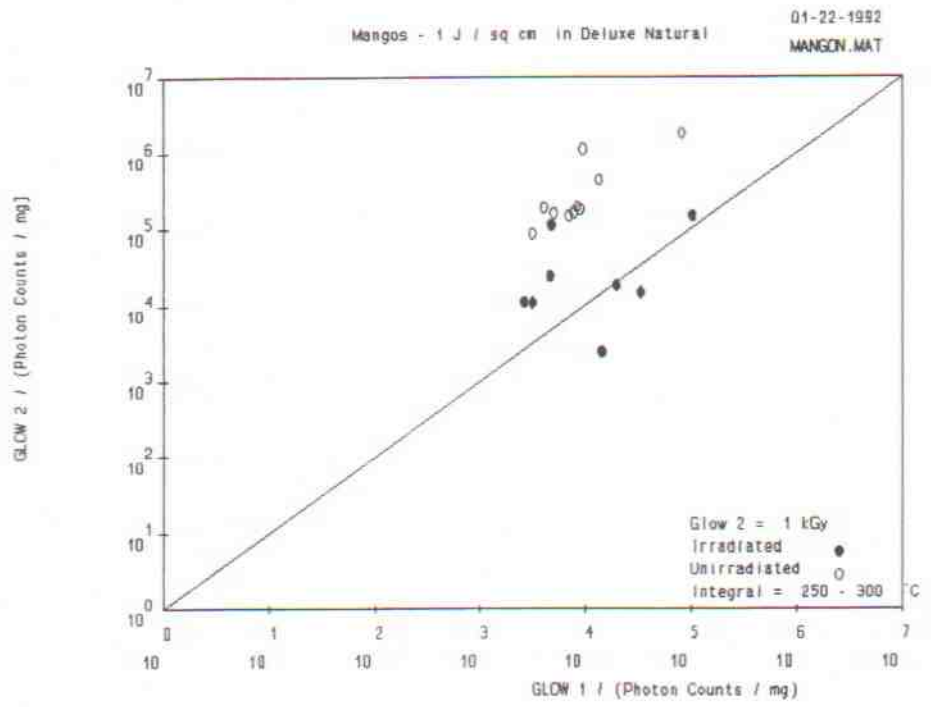

Figure 4.3.24 Concordance Plot for the 250-300°C Integral for Mangos in Deluxe Natural

4.4 Bleaching of TL from mangos - exposure dependence of signal loss

A second experiment was then defined to examine the dependence of signal loss on the extent of exposure. A second set of mangos was purchased for this experiment. Since the artificial daylight source was apparently more effective than natural deluxe, it was decided to use this lightbox to examine the effects of prolonged exposure.

A total of 100 mangos was chosen, 10 of which were left totally untreated to act as the unirradiated and unbleached controls. The remaining 90 mangos were individually wrapped in black plastic and irradiated in the Co-60 source for 45 minutes in six batches each containing 15 mangos. This resulted in radiation doses of the order of 0.75 kGy, recorded by dose mapping with Harwell Amber perspex dosimeters. 80 of these mangos were then split into 8 sets of 10 for bleaching as follows:

Batch	Bleaching Energy (Jcm^{-2})	Bleaching Time (s)
73	0	0
73/74	2	274
74	4	548
75	8	1096
75/76	16	2192
76	32	4384
78	64	8768
78/79	128	17536

Minerals from each set of mangos were then separated as outlined below.

Mineral Separation

The minerals from the mangos were separated in the following manner: Each mango was immersed in demineralised water and agitated in the ultrasonic bath for approximately 30

minutes. The mangos were then removed from the water, rinsed, and the residue left to stand for about 30 minutes. The surplus water was then decanted off, leaving behind enough to ensure that no mineral grains were lost. This was then transferred to a centrifuge tube and spun at 3000 rpm for a few minutes to force the mineral grains to the bottom to allow the rest of the water to be decanted off. The separation then followed procedure 7A from step 2, the addition of sodium polytungstate at a density of 1.7 gcm^{-3}.

TL Measurement

Each day light and dark counts were taken and a test TL ramp was performed in order to check for consistent operation of the TL reader on a day to day basis. All discs were read out on the Apple based single sample TL reader from ambient to 400 °C at a heating rate of 6 $°Cs^{-1}$. All discs were then irradiated to 1 kGy and the resulting TL was recorded as for the first glow, for the purpose of normalisation to account for sample to sample sensitivity variations. The average glow 1:glow 2 ratio for each summary file was calculated for a variety of temperature regions. Plots showing the resulting bleaching curve were prepared using Sigma Plot with regression analysis being based upon the sum of two exponential functions.

Absolute Signal Levels

The absolute mass normalised signal levels for glow 1 and glow 2 along with their ratios calculated for the integral 250-260 °C are shown in table 4.4.1.

Table 4.4.1

Filename (Apple)	Glow 1 250-260°C	Glow 2 250-260°C	Ratio G1 : G2	Notes
PB.2139.1/.2	0	(Lost)	-----	Blank
SP447.2140.1/.2	10094	3999054	0.003	Unirr
SP447.2141.1/.2	60500	11678967	0.005	
SP447.2142.1/.2	25750	3913308	0.007	
SP447.2143.1/.2	12248	1896872	0.006	
SP447.2144.1/.2	2605	2372572	0.001	
SP447.2145.1/.2	13246	4453539	0.003	
SP447.2146.1/.2	19745	2623305	0.008	
SP447.2147.1/.2	13875	3581725	0.004	
SP447.2148.1/.2	12650	3636496	0.003	
SP447.2149.1/.2	21927	3720241	0.006	
		Average ± SD	0.005 ± 0.002	

Filename (Apple)	Glow 1 250-260°C	Glow 2 250-260°C	Ratio G1 : G2	Notes
PB.2150.1/.2	0	2212	0	Blank
SP447.2151.1/.2	5976300	6227754	0.960	0 J
SP447.2152.1/.2	11436730	13386970	0.854	
SP447.2153.1/.2	4428625	5621692	0.788	
SP447.5154.1/.2	6626010	695670	0.952	
SP447.2155.1/.2	4845376	6287412	0.771	
SP447.2156.1/.2	3662534	3925734	0.933	
SP447.2157.1/.2	7873196	7315929	1.076	
SP447.2158.1/.2	2720883	3794363	0.717	
SP447.2159.1/.2	6832475	9228675	0.740	
SP447.2160.1/.2	7275032	8938814	0.814	
		Average ± SD	0.861 ± 0.116	
PB.2161.1/.2	3600	8450	0.426	Blank
SP447.2162.1/.2	11336780	12873630	0.881	2 J
SP447.2163.1/.2	33817825	40122375	0.843	
SP447.2164.1/.2	7990918	8903241	0.898	
SP447.2165.1/.2	1285095	1631465	0.788	
SP447.2166.1/.2	2951108	5680592	0.520	
SP447.2167.1/.2	3823321	6689714	0.572	
SP447.2168.1/.2	1835045	3007620	0.610	
SP447.2169.1/.2	773480	1046390	0.739	
SP447.2170.1/.2	5129057	5978957	0.858	
SP447.2171.1/.2	7534800	9915193	0.760	
		Average ± SD	0.747 ± 0.136	

Filename (Apple)	Glow 1 250-260°C	Glow 2 250-260°C	Ratio G1 : G2	Notes
PB.2172.1/.2	11450	80375	0.140	Blank
SP447.2173.1/.2	2213150	3014663	0.734	4 J
SP447.2174.1/.2	4325067	6508033	0.665	
SP447.2175.1/.2	1360893	2610339	0.521	
SP447.2176.1/.2	5018890	6247137	0.803	
SP447.2177.1/.2	1524892	1915850	0.796	
SP447.2178.1/.2	3450531	7629388	0.452	
SP447.2179.1/.2	3036740	6405480	0.474	
SP447.2180.1/.2	2195565	2981495	0.737	
SP447.2181.1/.2	4886863	6601291	0.740	
		Average ± SD	0.658 ± 0.139	
PB.2182.1/.2	5400	1028800	0.005	Blank
SP447.2183.1/.2	1544271	2231658	0.692	8 J
SP447.2184.1/.2	1422857	2778879	0.512	
SP447.2185.1/.2	1142742	3002121	0.381	
SP447.2186.1/.2	3375164	5477543	0.616	
SP447.2187.1/.2	215054	1708958	0.126	****
SP447.2188.1/.2	1167475	4136688	0.282	
SP447.2189.1/.2	6205475	10296800	0.603	
SP447.2190.1/.2	5842171	7422186	0.787	
SP447.2191.1/.2	1736550	3786008	0.459	
SP447.2192.1/.2	3171650	6628980	0.478	
		Average ± SD	0.534 ± 0.157	

Filename (Apple)	Glow 1 250-260°C	Glow 2 250-260°C	Ratio G1 : G2	Notes
PB.2193.1/.2	0	3200	0	Blank
SP447.2194.1/.2	3487863	9084363	0.384	16 J
SP447.2195.1/.2	4094780	10174040	0.402	
SP447.2196.1/.2	4230910	7031105	0.602	
SP447.2197.1/.2	2824578	7010089	0.403	
SP447.2198.1/.2	2870150	6331092	0.453	
SP447.2199.1/.2	2092450	4583500	0.457	
SP447.2200.1/.2	5771581	14923356	0.387	
SP447.2201.1/.2	3516450	7282417	0.483	
SP447.2202.1/.2	3758983	6844875	0.549	
SP447.2203.1/.2	2306993	3892329	0.593	
		Average ± SD	0.471 ± 0.083	
PB.2204.1/.2	0	500	0	Blank
SP447.2205.1/.2	3314350	5870963	0.565	32 J
SP447.2206.1/.2	11237900	21901063	0.513	
SP447.2207.1/.2	824985	1757945	0.469	
SP447.2208.1/.2	1927175	6460713	0.298	
SP447.2209.1/.2	3412950	6801518	0.502	
SP447.2210.1/.2	2970200	5928817	0.501	
SP447.2211.1/.2	4163750	9288750	0.448	
SP447.2212.1/.2	7498771	14710200	0.510	
SP447.2213.1/.2	2941565	5387850	0.546	
		Average ± SD	0.484 ± 0.078	

Filename (Apple)	Glow 1 250-260 °C	Glow 2 250-260 °C	Ratio G1 : G2	Notes
PB.2214.1/.2	83	650	0.128	Blank
SP447.2215.1/.2	2072881	4445963	0.466	64 J
SP447.2216.1/.2	9888163	14300725	0.691	
SP447.2217.1/.2	3241571	5476121	0.592	
SP447.2218.1/.2	7230000	5550600	1.303	****
SP447.2219.1/.2	1944975	4494863	0.433	
SP447.2220.1/.2	8030000	12856900	0.625	
SP447.2221.1/.2	5247925	7128550	0.736	
SP447.2222.1/.2	6425383	9911983	0.648	
SP447.2223.1/.2	6785908	6827911	0.994	****
SP447.2224.1/.2	1613505	2770398	0.582	
		Average ± SD	0.597 ± 0.104	
PB.2225.1/.2	0	3175	0	Blank
SP447.2226.1/.2	2295907	6286179	0.365	128 J
SP447.2227.1/.2	1899025	6456613	0.294	
SP447.2228.1/.2	549700	1627507	0.338	
SP447.2229.1/.2	1210821	4046286	0.299	
SP447.2230.1/.2	2312565	8384920	0.299	
SP447.2231.1/.2	7072542	14938117	0.473	
SP447.2232.1/.2	1282946	4022673	0.319	
SP447.2233.1/.2	1210244	4595178	0.263	
SP447.2234.1/.2	4071634	5306182	0.767	
SP447.2235.1/.2	424217	1820646	0.283	
		Average ± SD	0.363 ± 0.157	

*** Note:- These glow curves were excluded from the statistical analysis as they were obvious outliers to the distribution.

4.5 Results and Discussion

The average ratios for three different temperature regions (150-250°C, 180-200°C and 200-220°C) were calculated and plotted with regression analysis being performed based on the sum of two exponential functions as shown below;

$$F(x) = A \exp(-Bx) + C \exp(-Dx)$$

The results are shown in the following tables and graphs;

Bleaching Results for 150-250°C

Bleaching Energy (Jcm^{-2})	Glow 1 : Glow 2 Ratio ($\pm$ SE)	Regression Coefficients	Predicted Values	% Residuals
Unirradiated	0.0009 $\pm$ 0.0001	-----	-----	-----
0	0.583 $\pm$ 0.001	A = 0.2665	0.590	-1.1
2	0.500 $\pm$ 0.002	B = 0.2276	0.492	1.7
4	0.440 $\pm$ 0.004	C = 0.3236	0.429	2.4
8	0.352 $\pm$ 0.004	D = 0.0013	0.364	-3.3
16	0.298 $\pm$ 0.001		0.324	-8.1
32	0.313 $\pm$ 0.001		0.311	0.5
64	0.344 $\pm$ 0.002		0.298	15.4
128	0.254 $\pm$ 0.004		0.275	-7.7

Bleaching Results for 180-200 °C

Bleaching Energy (Jcm^{-2})	Glow 1 : Glow 2 Ratio ($\pm$ SE)	Regression Coefficients	Predicted Values	% Residuals
Unirradiated	0.0005 $\pm$ 0.0001	-----	-----	-----
0	0.681 $\pm$ 0.002	A = 0.2980	0.688	-1.1
2	0.589 $\pm$ 0.003	B = 0.2180	0.581	1.2
4	0.528 $\pm$ 0.002	C = 0.3904	0.513	3.1
8	0.423 $\pm$ 0.005	D = 0.0016	0.438	-3.4
16	0.358 $\pm$ 0.001		0.390	-8.1
32	0.367 $\pm$ 0.002		0.372	-1.1
64	0.418 $\pm$ 0.003		0.353	18.4
128	0.290 $\pm$ 0.005		0.319	-9.3

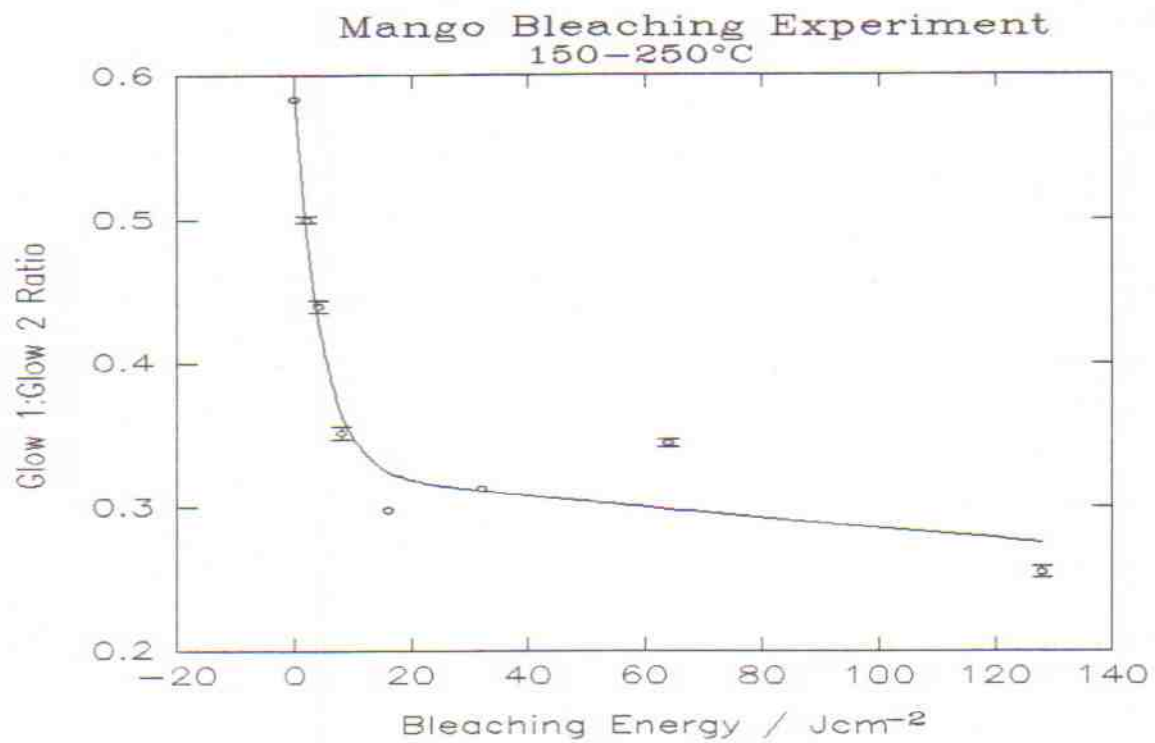

Figure 4.5.1 - Bleaching Curve for 150-250 °C Integral

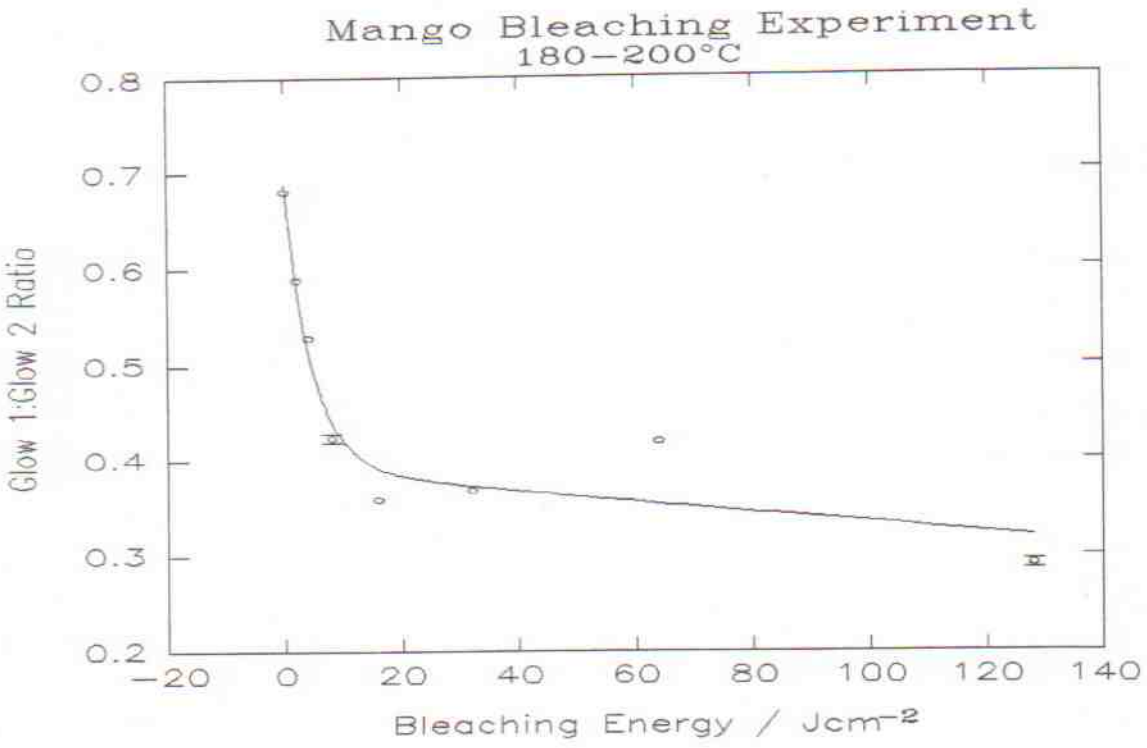

Figure 4.5.2 - Bleaching Curve for the 180-200°C Integral

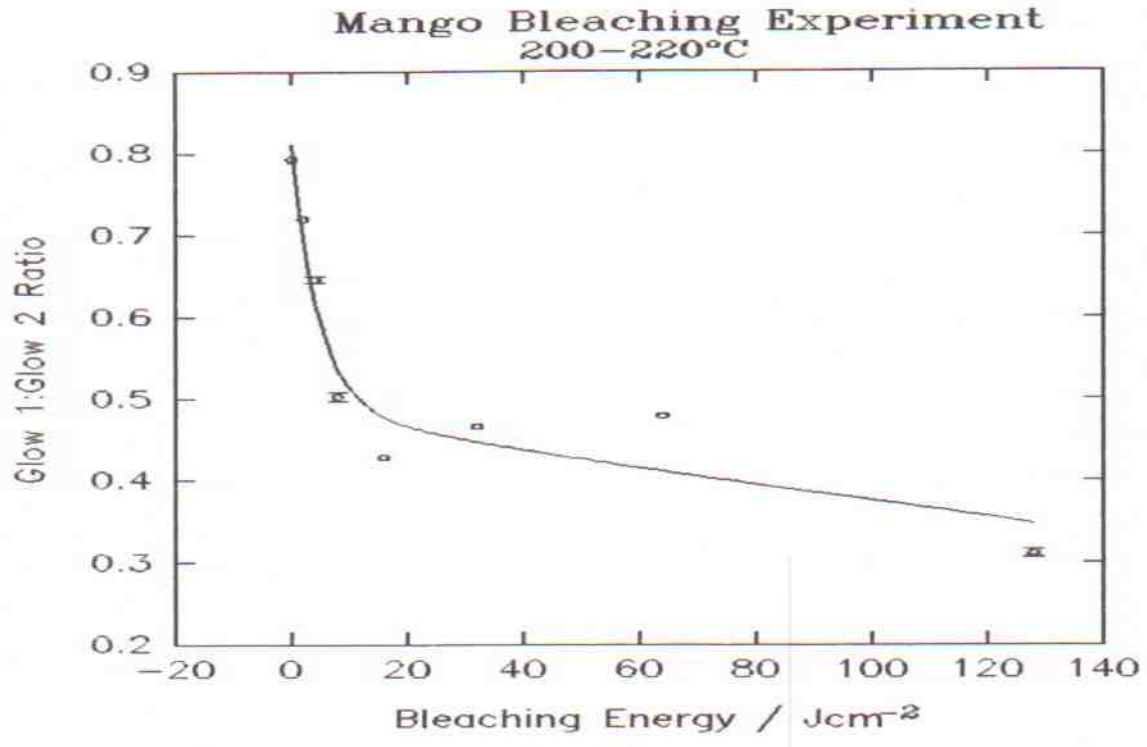

Figure 4.5.3 - Bleaching Curve for the 200-220°C Integral

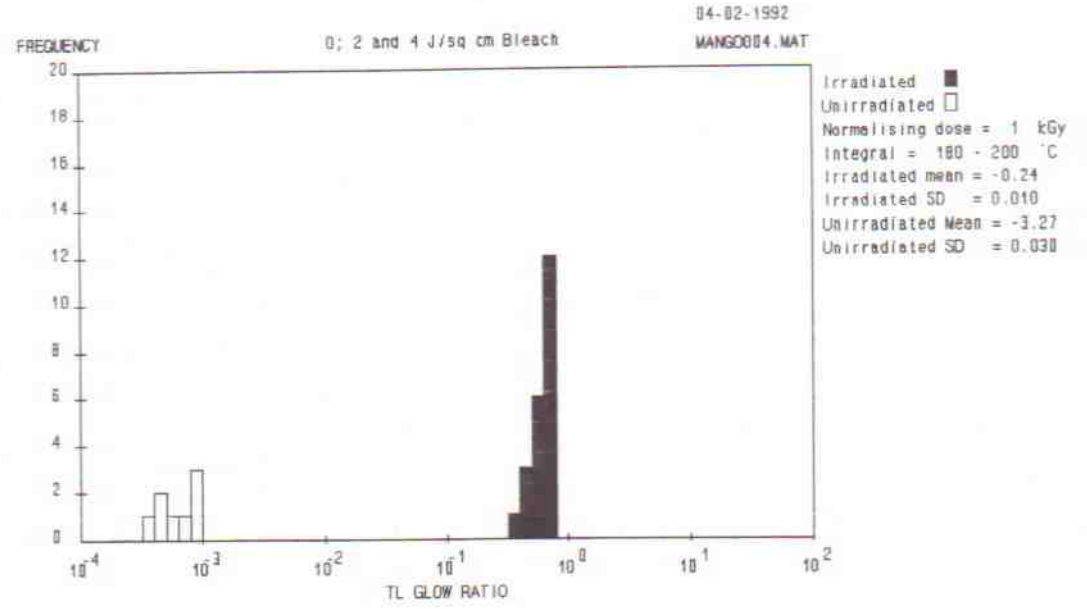

Figure 4.5.4 - Glow Ratio Histogram showing the Unirradiated Controls and the samples after 0, 2 and 4 Jcm^{-2} Bleaching

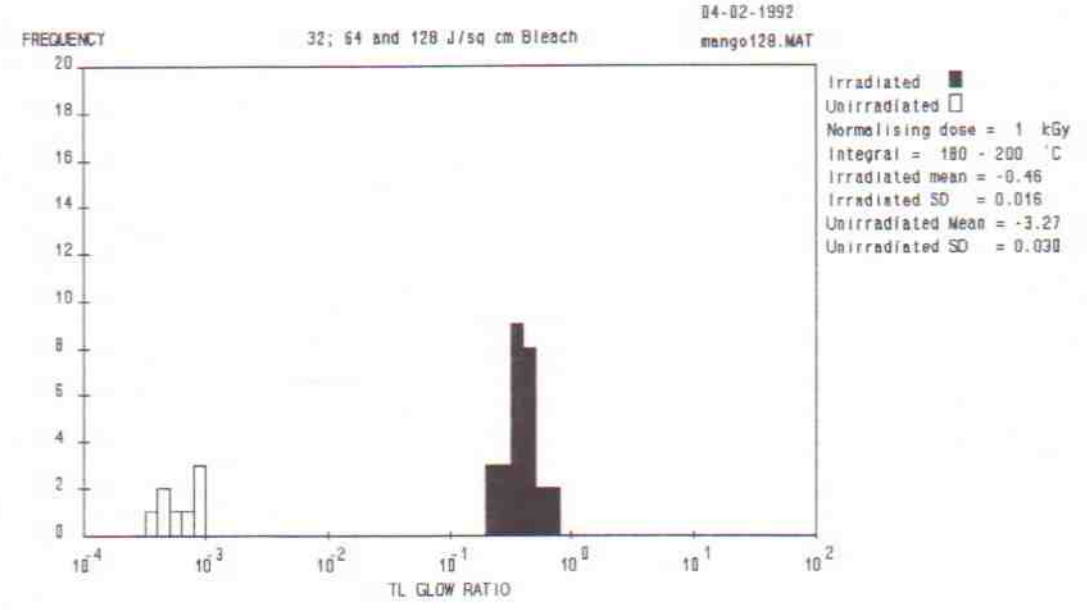

Figure 4.5.5 - Glow Ratio Histogram showing the Unirradiated Controls and the samples after 32, 64 and 128 Jcm^{-2} Bleach

As can be seen from the graphs, there would appear to two distinct regions, the first to about 10 Jcm^{-2} where there is a rapid bleaching, and then a second region of much slower bleaching indicative of perhaps reaching a residual level that would not be significantly changed even after very much longer bleaching times. For each temperature band, the residual level after 128 Jcm^{-2} is seen to be very much greater (i.e. 2-3 orders of magnitude) than the average unirradiated glow ratio signifying that with these samples at least, all of the mangos (even after the longest bleaching) would be easily identifiable as being irradiated. This is shown in Figure 4.5.4 and Figure 4.5.5 where it can be seen that the blank and irradiated distributions are well separated.

There are three possible reasons for the non single exponential nature of the bleaching curve;

(1) - Distribution of traps. It is known that with feldspar and feldspar dominated polymineral samples, there exists a distribution of traps between the unstable and geological signals. Hence the less stable signal could be being bleached more efficiently than the more stable, thus giving rise to the residual level. This should be shown up by a shift to higher temperature of the initial rise of the glow curve.

(2) - Non first order kinetics. It has been demonstrated in PSL studies and modelling that there is doubt as to whether the bleaching curve should exhibit first order kinetics. It is postulated in this research that even a single trap / centre luminescence model will exhibit non first order kinetics once retrapping is taken into account. The occurrence of retrapping is thought to be much more likely in PSL due to the thermal residence mean life at the measurement temperature.

(3) - Polychromatic light. The light source used to generate the bleaching in this experiment is a polychromatic fluorescent tube (Artificial daylight) and thus there will be wavelengths with differing probabilities of evicting the same trapped charge carriers.

Glow shape analysis.

Analysis of the glow shapes can yield important information on the bleaching process. The

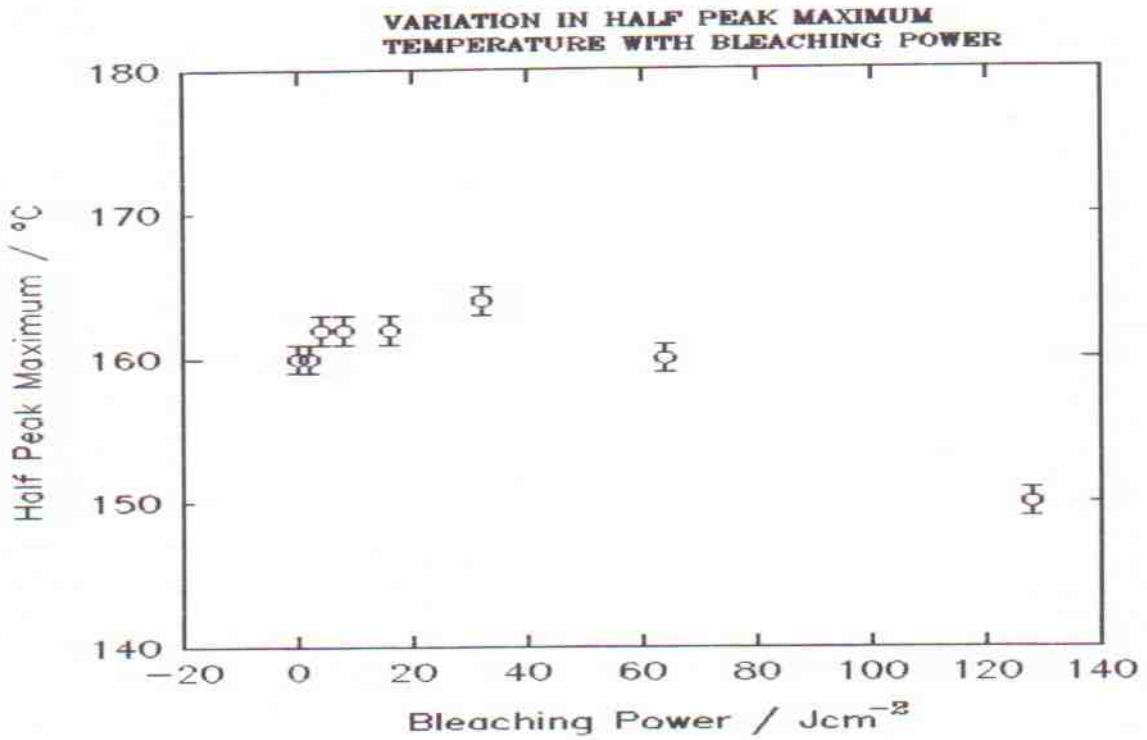

Figure 4.5.6 - Variation in the initial rise half maximum temperature as an indicator of whether there is sequential bleaching of traps increasing in depth.

first criterion shown is the position of the first glow peak half maximum, this can be seen in Figure 4.5.6 which depicts the half maximum temperature from an average glow curve. As can be seen from this graph, there appears to be no significant shift in the peak position to higher temperature as one might expect if shallower traps were being bleached before deeper ones. The only significant peak shift is in the 128 Jcm^{-2} glow curve which shows a 10 $^{\circ}C$ peak shift to *lower* temperature. This can not be explained in terms of bleaching and is more likely to be an experimental artifact arising from a different thermal contact. This shift to lower temperatures may well have contributed to the lower glow ratios as seen for this point in the bleaching curves.

Another indicator of the effect of the bleaching is the modification (if any) to the overall

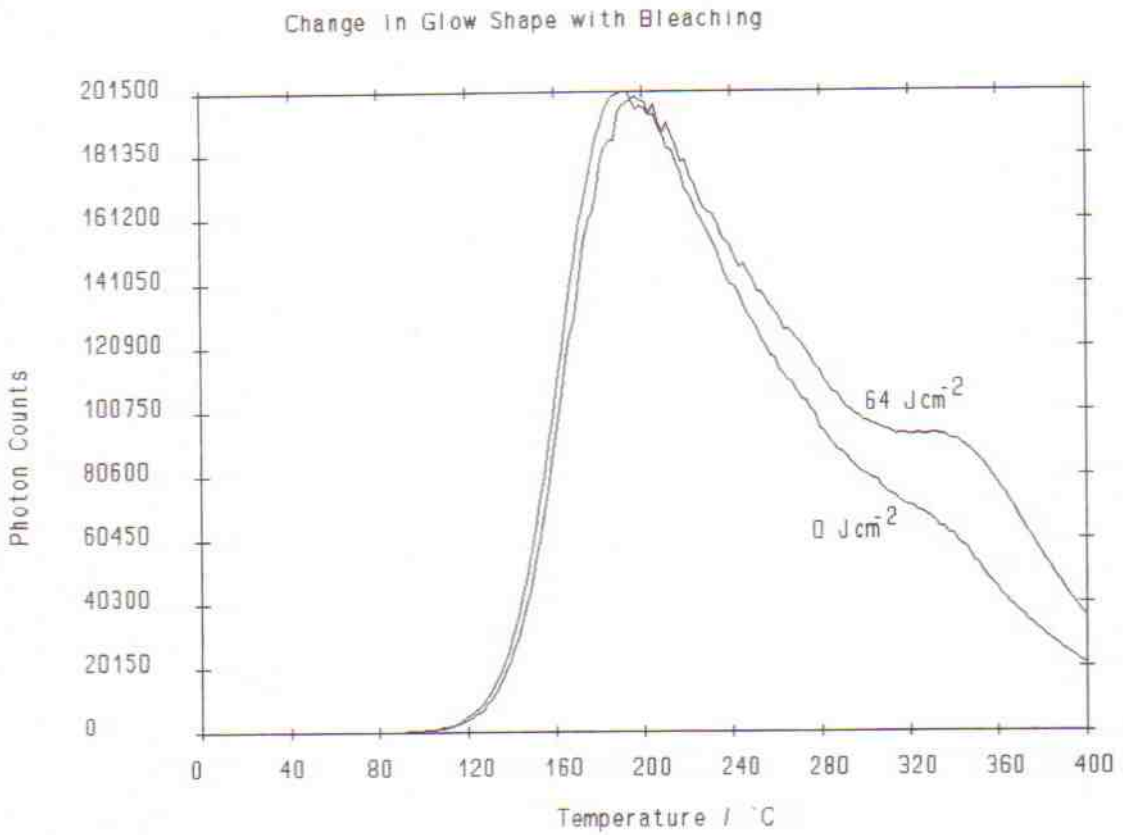

Figure 4.5.7 - TL Glow Curves after 0 and 64 Jcm^{-2} Bleaching

structure of the glow curve. Such a modification can be seen in Figure 4.5.7 below between the average unbleached glow curve and the average glow curve after 64 Jcm^{-2} bleaching. As can be seen, the bleached curve has a resolved peak at around 350°C, whereas in the unbleached glow curve this is merely an inflection, thus demonstrating that the sub 300°C glow curve is bleached relative to the glow curve above 300°C.

From the above results it would seem that there is a residual component of the TL glow curve even after a high degree of bleaching. This residual TL signal yields glow ratios 2-3 orders of magnitude greater than those resulting from the unirradiated controls used in this experiment. Thus on this basis all of the bleached samples examined here would have been readily identifiable as having been irradiated.

5 Conclusions

The need for detection methods had clearly been established at a time of growing international trade in irradiated products. The thermoluminescence technique had been developed to a high level of reliability. TL measurements had been used for unambiguous qualitative identification of herbs and spices in particular. This project set as its aims; the development of the TL procedure for herbs and spices, the preparation of a formal protocol for detecting irradiated herbs and spices, the extension ot the TL procedure to fruits and vegetables and an assessment of the post irradiation stability of the TL signal under illumination. It has been successful in achieving all of the above.

Developmental work on the density separation method has resulted in the incorporation of pre-concentration steps to enhance the sensitivity of the TL signal, particularly, where the separation technique resulted in low mineral yield for commercially clean samples. This has resulted in an order of magnitude increase in the absolute, TL, signal levels and provides a means of obtaining larger quantities of minerals for any further quantification, thus reducing the ambiguity of interpretation of data.

An interlaboratory trial was organised at SURRC jointly with the Berlin Federal Health Office, involving 8 european laboratories of diverse levels of experience. A set of reference materials and paired (irradiated and unirradiated) samples of 12 commercial grade herbs and spices was supplied to each laboratory. They were then asked to conduct instrumental checks and then, to follow a full sodium polytungstate density separation protocol for mineral separation. Duplicate TL glow curves were recorded for each sample; one initial or "first glow" and another following a renormalisation dose of 1 kGy. The data obtained were integrated into 25 $^{\circ}$C bands and reported throughout the glow curve, so that differences could be taken into account in the analysis. Despite the diversity of experience and equipment employed results from all laboratories showed that it was possible to determine which samples were irradiated. This demonstrated that the separation method could be successfully adopted in other laboratories and the procedure was formally recognised, by MAFF, for detection of irradiated food for enforcement of UK legislation. The published protocol for detecting irradiated herbs and spices defines a number of quality assurance checks which should be

conducted. Blank levels should be measured for all glassware and reagents and used to define minimum detectable levels. Duplicate analyses, of first and renormalisation glows, should be made for each sample, using a full separation method and checked for concordance. Only analyses with second glow sensitivity greater than 10 times the minimum detectable level are accepted. This enables the detection of glow ratios below 0.1, from all valid measurements to allow for secure identification of all unirradiated samples.

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A set of illumination studies were conducted to investigate and implications of this optical bleaching effect. Two experimental light boxes were constructed; each 2 m x 50 x 50 cm, containing four fluorescent tubes. Since fruits and vegetables are handled in both natural and artificial lights, the decision was made to concentrate on "Artificial daylight" and "Natural Deluxe" tubes. "Artificial daylight" tubes produce a broad spectrum with some line superposition extending into the the near UV; whereas "Natural Deluxe" is a warmer spectrum used to enhance foods on display in shops. The light boxes were painted internally with TiO_2 reflector paint and the uniformity was mapped using a photodiode. Thereafter a molectron PR 500 pyroelectric radiometer was used to measure the absolute 2 pi energy fluence across the whole spectrum. For the two boxes the energy fluences of 7.3 and 7.7 mW cm^{-2} respectively, were obtained.

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4.5 Results and Discussion

The average ratios for three different temperature regions (150-250°C, 180-200°C and 200-220°C) were calculated and plotted with regression analysis being performed based on the sum of two exponential functions as shown below;

$$F(x) = A \exp(-Bx) + C \exp(-Dx)$$

The results are shown in the following tables and graphs;

Bleaching Results for 150-250°C

Bleaching Energy (Jcm^{-2})	Glow 1 : Glow 2 Ratio ($\pm$ SE)	Regression Coefficients	Predicted Values	% Residuals
Unirradiated	0.0009 $\pm$ 0.0001	-----	-----	-----
0	0.583 $\pm$ 0.001	A = 0.2665	0.590	-1.1
2	0.500 $\pm$ 0.002	B = 0.2276	0.492	1.7
4	0.440 $\pm$ 0.004	C = 0.3236	0.429	2.4
8	0.352 $\pm$ 0.004	D = 0.0013	0.364	-3.3
16	0.298 $\pm$ 0.001		0.324	-8.1
32	0.313 $\pm$ 0.001		0.311	0.5
64	0.344 $\pm$ 0.002		0.298	15.4
128	0.254 $\pm$ 0.004		0.275	-7.7

Bleaching Results for 180-200°C

Bleaching Energy (Jcm^{-2})	Glow 1 : Glow 2 Ratio (± SE)	Regression Coefficients	Predicted Values	% Residuals
Unirradiated	0.0005 ± 0.0001	-----	-----	-----
0	0.681 ± 0.002	A = 0.2980	0.688	-1.1
2	0.589 ± 0.003	B = 0.2180	0.581	1.2
4	0.528 ± 0.002	C = 0.3904	0.513	3.1
8	0.423 ± 0.005	D = 0.0016	0.438	-3.4
16	0.358 ± 0.001		0.390	-8.1
32	0.367 ± 0.002		0.372	-1.1
64	0.418 ± 0.003		0.353	18.4
128	0.290 ± 0.005		0.319	-9.3

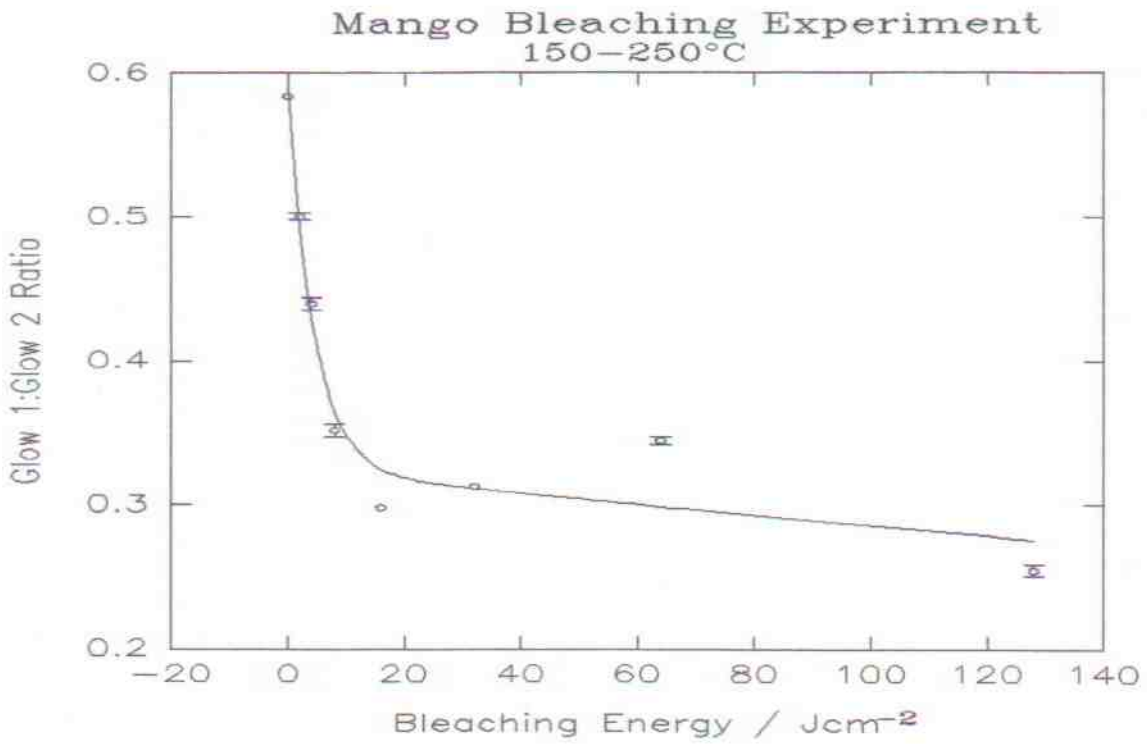

Figure 4.5.1 - Bleaching Curve for 150-250°C Integral

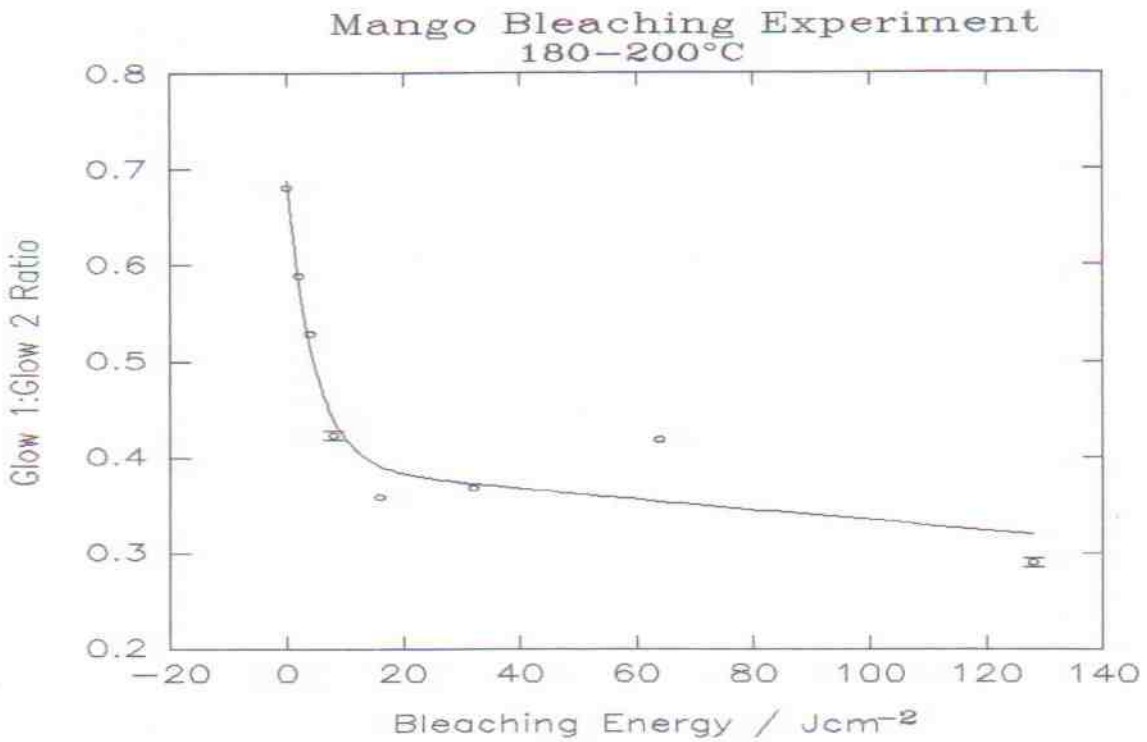

Figure 4.5.2 - Bleaching Curve for the 180-200°C Integral

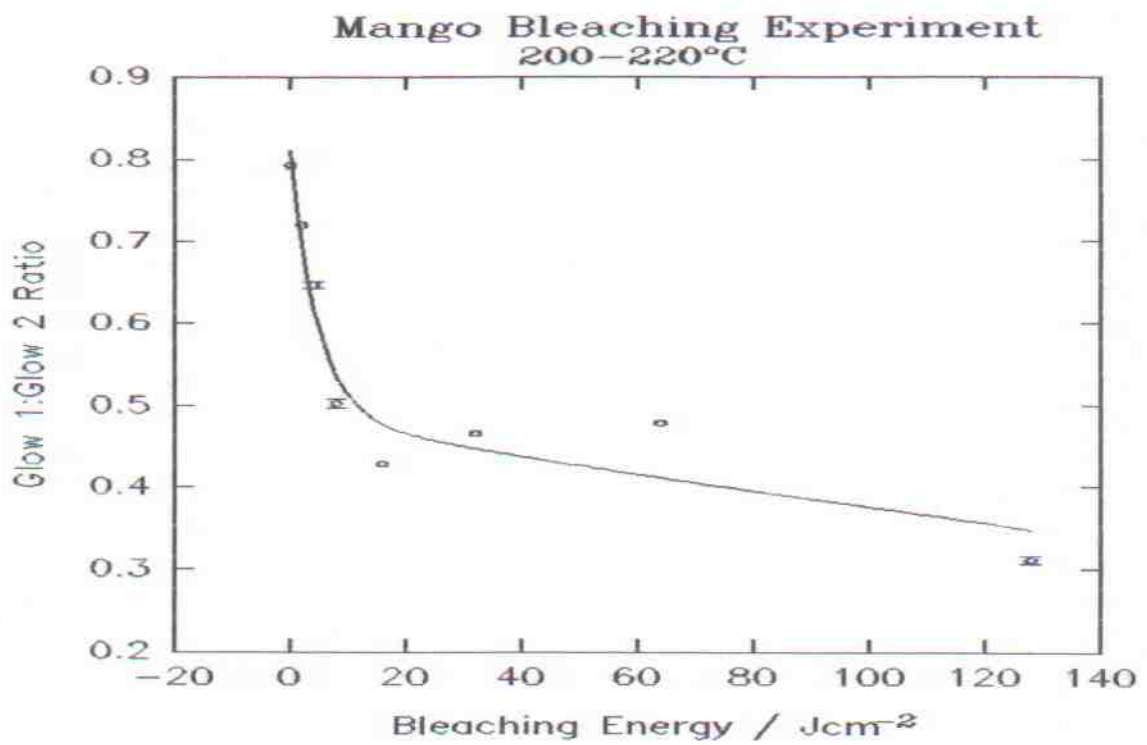

Figure 4.5.3 - Bleaching Curve for the 200-220°C Integral

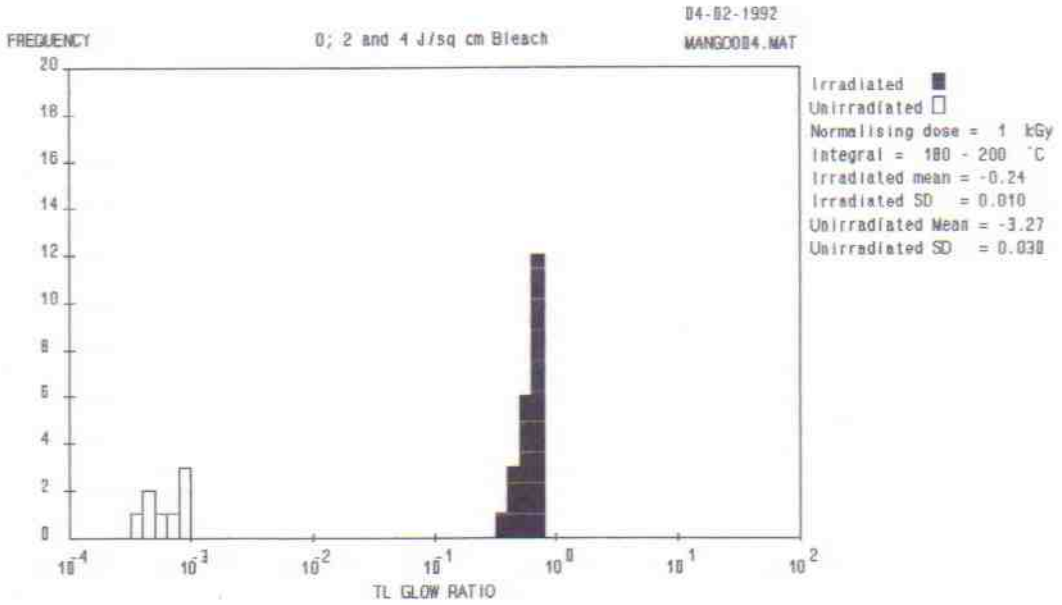

Figure 4.5.4 - Glow Ratio Histogram showing the Unirradiated Controls and the samples after 0, 2 and 4 Jcm^{-2} Bleaching

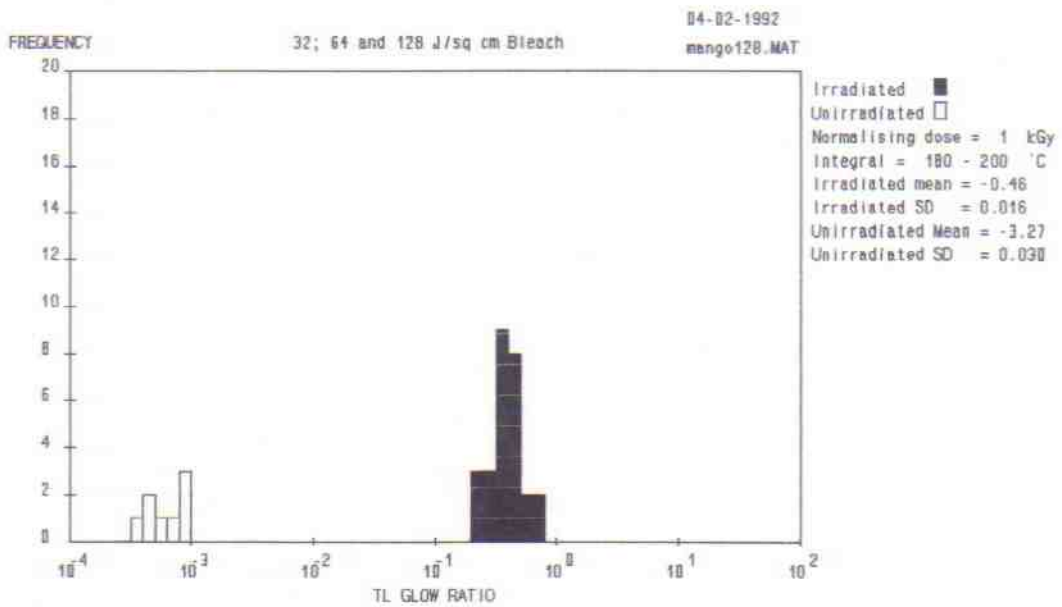

Figure 4.5.5 - Glow Ratio Histogram showing the Unirradiated Controls and the samples after 32, 64 and 128 Jcm^{-2} Bleach

As can be seen from the graphs, there would appear to two distinct regions, the first to about 10 Jcm^{-2} where there is a rapid bleaching, and then a second region of much slower bleaching indicative of perhaps reaching a residual level that would not be significantly changed even after very much longer bleaching times. For each temperature band, the residual level after 128 Jcm^{-2} is seen to be very much greater (i.e. 2-3 orders of magnitude) than the average unirradiated glow ratio signifying that with these samples at least, all of the mangos (even after the longest bleaching) would be easily identifiable as being irradiated. This is shown in Figure 4.5.4 and Figure 4.5.5 where it can be seen that the blank and irradiated distributions are well separated.

There are three possible reasons for the non single exponential nature of the bleaching curve;

(1) - Distribution of traps. It is known that with feldspar and feldspar dominated polymineral samples, there exists a distribution of traps between the unstable and geological signals. Hence the less stable signal could be being bleached more efficiently than the more stable, thus giving rise to the residual level. This should be shown up by a shift to higher temperature of the initial rise of the glow curve.

(2) - Non first order kinetics. It has been demonstrated in PSL studies and modelling that there is doubt as to whether the bleaching curve should exhibit first order kinetics. It is postulated in this research that even a single trap / centre luminescence model will exhibit non first order kinetics once retrapping is taken into account. The occurrence of retrapping is thought to be much more likely in PSL due to the thermal residence mean life at the measurement temperature.

(3) - Polychromatic light. The light source used to generate the bleaching in this experiment is a polychromatic fluorescent tube (Artificial daylight) and thus there will be wavelengths with differing probabilities of evicting the same trapped charge carriers.

Glow shape analysis.

Analysis of the glow shapes can yield important information on the bleaching process. The

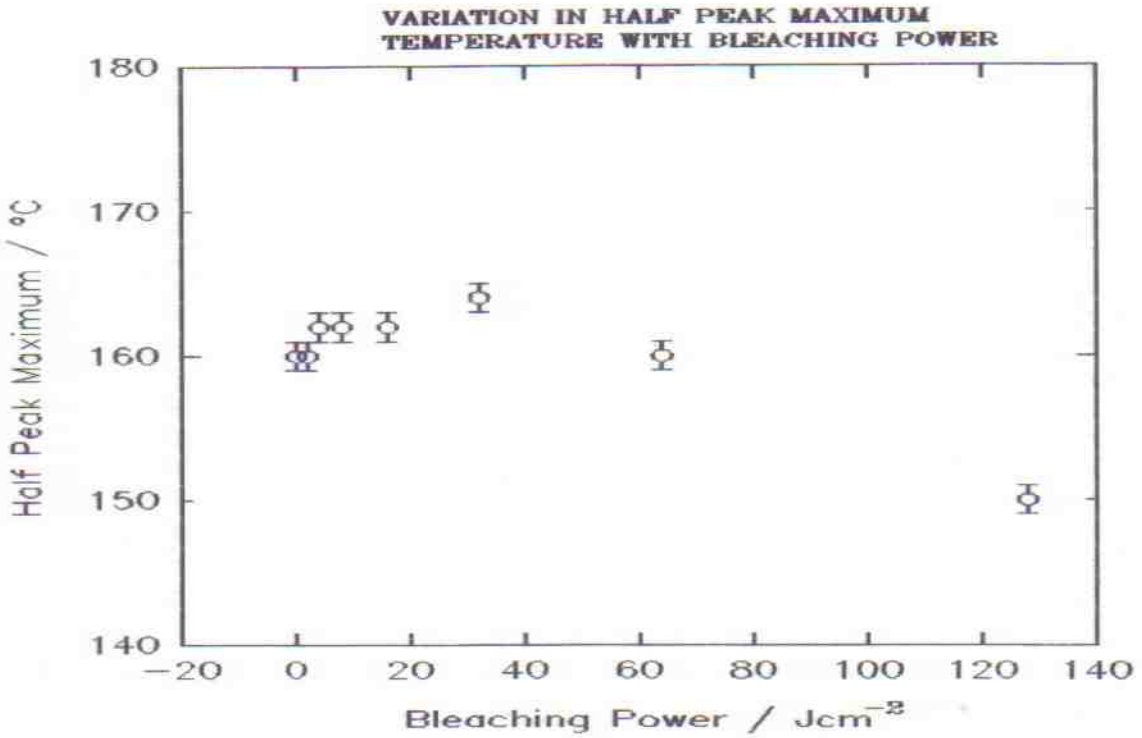

Figure 4.5.6 - Variation in the initial rise half maximum temperature as an indicator of whether there is sequential bleaching of traps increasing in depth.

first criterion shown is the position of the first glow peak half maximum, this can be seen in Figure 4.5.6 which depicts the half maximum temperature from an average glow curve. As can be seen from this graph, there appears to be no significant shift in the peak position to higher temperature as one might expect if shallower traps were being bleached before deeper ones. The only significant peak shift is in the 128 Jcm^{-2} glow curve which shows a 10 $^{\circ}C$ peak shift to *lower* temperature. This can not be explained in terms of bleaching and is more likely to be an experimental artifact arising from a different thermal contact. This shift to lower temperatures may well have contributed to the lower glow ratios as seen for this point in the bleaching curves.

Another indicator of the effect of the bleaching is the modification (if any) to the overall

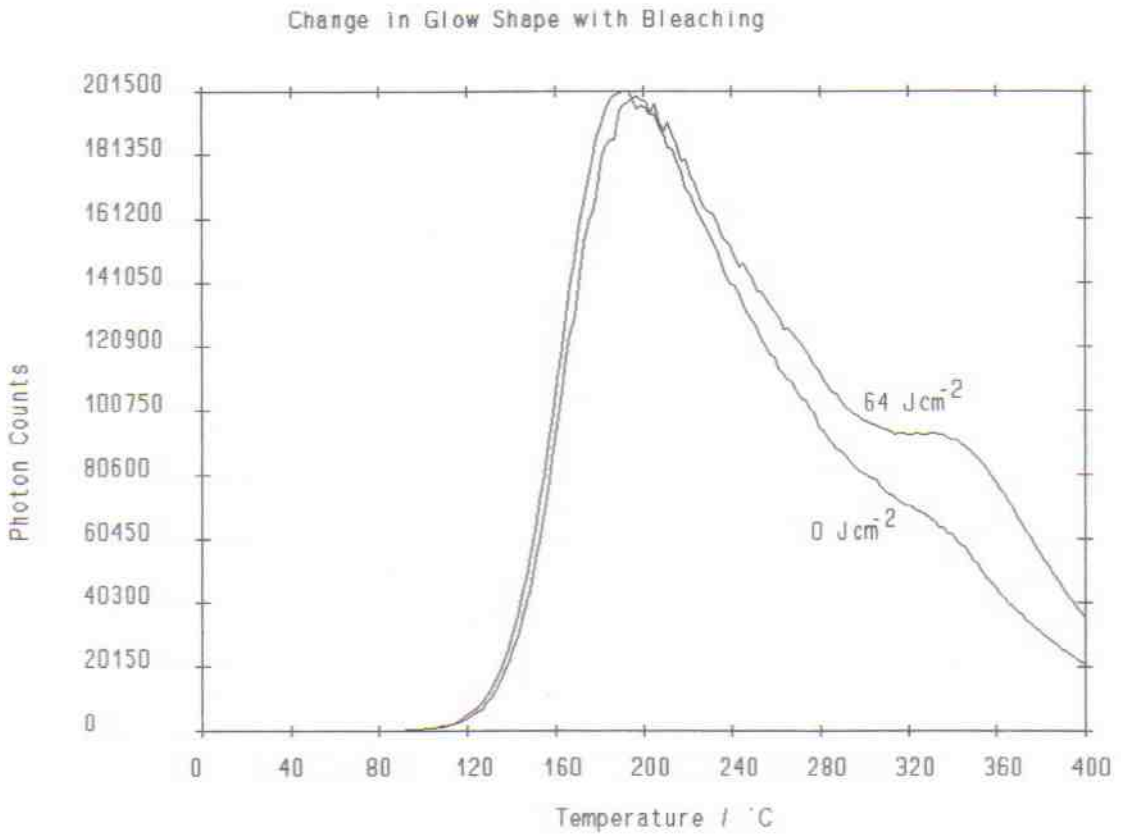

Figure 4.5.7 - TL Glow Curves after 0 and 64 Jcm^{-2} Bleaching

structure of the glow curve. Such a modification can be seen in Figure 4.5.7 below between the average unbleached glow curve and the average glow curve after 64 Jcm^{-2} bleaching. As can be seen, the bleached curve has a resolved peak at around 350°C, whereas in the unbleached glow curve this is merely an inflection, thus demonstrating that the sub 300°C glow curve is bleached relative to the glow curve above 300°C.

From the above results it would seem that there is a residual component of the TL glow curve even after a high degree of bleaching. This residual TL signal yields glow ratios 2-3 orders of magnitude greater than those resulting from the unirradiated controls used in this experiment. Thus on this basis all of the bleached samples examined here would have been readily identifiable as having been irradiated.

4.5 Discussion

In this section the results of two experiments were reported which demonstrate that post-irradiation optical exposure effects the levels of residual TL remaining. Two light boxes based on common display spectral sources were constructed and used to investigate the bleaching of mangos.

The important findings of these experiments are that optical bleaching does reduce the signal level, but that the losses resulting from prolonged exposure occur at a much diminished rate compared with initial losses, providing support for the concept of a residual "unbleachable" component, which in the cases examined here could account for up to 40-50% of initial signal levels. Clearly the impact of such signal losses on TL identification rates depends on initial background levels, and it is notable in these experiments with tenfold replication that the mnean levels were still well distinguished between irradiated and unirradiated samples. Therefore bleaching may not in fact prove to be an obstacle to detecting many irradiated fruits and vegetables, although it's effect on quantitative response can not be overlooked.

5 Conclusions

The need for detection methods had clearly been established at a time of growing international trade in irradiated products. The thermoluminescence technique had been developed to a high level of reliability. TL measurements had been used for unambiguous qualitative identification of herbs and spices in particular. This project set as its aims; the development of the TL procedure for herbs and spices, the preparation of a formal protocol for detecting irradiated herbs and spices, the extension ot the TL procedure to fruits and vegetables and an assessment of the post irradiation stability of the TL signal under illumination. It has been successful in achieving all of the above.

Developmental work on the density separation method has resulted in the incorporation of pre-concentration steps to enhance the sensitivity of the TL signal, particularly, where the separation technique resulted in low mineral yield for commercially clean samples. This has resulted in an order of magnitude increase in the absolute, TL, signal levels and provides a means of obtaining larger quantities of minerals for any further quantification, thus reducing the ambiguity of interpretation of data.

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